

R. COSIMATI*[#], DANIELE MARI***EFFECTS OF PRECIPITATION HARDENING IN Co-Ni-Cr ALLOY ON DISSIPATIVE MOTION OF DISLOCATIONS BY AMPLITUDE-DEPENDENT INTERNAL FRICTION MEASUREMENTS****WPLYW UTWARDZENIA WYDZIELENIOWEGO STOPU CO-NI-CR NA ROZPRASZAJĄCY RUCH DYSLOKACJI BADANY PRZEZ ZALEŻNE OD AMPLITUDY POMIARY TARCIA WEWNĘTRZNEGO**

The effects of precipitation hardening occurring in a Co-Ni-Cr alloy after annealing treatments have been studied by using mechanical spectroscopy. The amplitude-dependent internal friction (ADIF) due to the dissipative motion of dislocations reveals the presence of a threshold strain for weakly pinned dislocations. The change of ADIF curves and the increase of the elastic modulus after thermal cycles producing precipitates suggest that dislocations motion is hindered leading to increasing strength of the material. Precipitation is confirmed by the changes of thermoelectric power (TEP) and by hardness measurements showing a hardness increase at the same temperature as the maximum in TEP curve. The ADIF spectra as well as the interaction between dislocations and precipitates are interpreted by proposing a phenomenological model based on the Granato-Lücke theory.

Keywords: Precipitation, thermoelectric power, strain amplitude, Granato-Lücke theory

Wpływ utwardzania wydzieleniowego występującego w stopie Co-Ni-Cr po wyżarzaniu zbadano za pomocą spektroskopii mechanicznej. Wewnętrzne tarcie zależne od amplitudy (ADIF) ze względu na rozpraszający ruch dyslokacji ujawnia obecność naprężenia granicznego dla słabo zakotwiczonych dyslokacji. Zmiana krzywych ADIF i wzrost modułu sprężystości po obróbce cieplnej wytwarzającej wydzielenia wskazują, że ruch dyslokacji jest utrudniony prowadząc do zwiększenia wytrzymałości materiału. Wydzielenia są potwierdzone przez zmiany siły termoelektrycznej i pomiary twardości, wykazujące zwiększenie twardości w tej samej temperaturze, co maksimum na krzywej TEP. Widma ADIF, a także oddziaływania między dyslokacjami i wydzieleniami są interpretowane przez proponowany fenomenologiczny model oparty na teorii Granato-Lücke.

1. Introduction

Some alloys based on Cobalt-Nickel-Chrome exhibit remarkably high values of hardness and strength combined with an excellent corrosion resistance. For this reason they find place in a wide range of applications from aerospace industry to orthopedic implants [1]. The mechanical properties of these materials can be improved or modified by thermo-mechanical treatments. Several experimental studies [2-5] on commercial cobalt-nickel based super-alloys (e.g. MP35N or MP159) have claimed the existence of two mechanisms of hardening. In fact, in addition to the main strain hardening due to the cold-work of the material, a supplementary hardening can be produced by aging the material after deformation [3]. The origin of the primary strain hardening for multiphase alloys with the Co:Ni ratio greater than 45:25 is attributed to the γ (f.c.c.) \rightarrow ϵ (h.c.p.) martensitic transformation induced by plastic deformation [4]. On the other hand, the conclusions about the microstructural origin of the secondary hardening are slightly divergent taking into account alternative mechanisms as precipitation,

solute partitioning or segregation of solute atoms to stacking faults formed during deformation [3,5]. Nevertheless, it is well known that hardness strongly depends on the mobility of dislocations. Mechanical spectroscopy and amplitude-dependent internal friction (ADIF) measurements have proven to be a very sensitive tool for studying dislocations-point defect interaction mechanisms [6]. In this paper, different techniques are used to investigate the secondary hardening mechanism in a Co-Ni-Cr alloy and its effect on the dissipative motion of dislocations. Besides mechanical spectroscopy, thermoelectric power (hereafter referred to as TEP) is used to assess the content of solute atoms [7], whilst hardness tests provided an indication of the material properties, such as strength, ductility and wear resistance [8].

On the base of the experiments presented in this study, we envisage that the aforementioned secondary hardening can be attributed to a fine dispersion of nano-sized precipitates, coherent with the matrix, which act as strong pinning points for dislocations and hinder their motion increasing the yield strength of the alloy. A phenomenological model based on

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the Granato-Lücke theory for dislocation pinning-depinning is proposed to interpret the effects of such precipitation on mechanical loss due to the dissipative motion of dislocations.

2. Experimental

The base material was a Co-Ni-Cr based alloy received as cold-drawn rods ultimately annealed at a diameter of 2.6 mm before being drawn to 1.85 mm. Atomic concentrations of alloy's elements ranged as reported: Co 45-50, Ni 20-25, Cr 15-20. Other elements added in minor concentration to the base composition were Fe, Mo and Ti. As received (AR) samples were initially cut from the rods. Solution treated (ST) samples were annealed to homogenize the microstructure at 1200°C during 5 minutes under a moderate flow of Argon and rapidly cooled by quenching in water. Cold worked (CW) samples were finally laminated at 50% of the cross section.

Measurements of internal friction and dynamic modulus were carried out both on CW and ST samples by means of a free inverted torsion pendulum at a frequency of about 1 Hz. Internal friction was calculated from the logarithmic decrement of free oscillations according to the expression $Q^{-1} = (1/n\pi) \cdot \ln(A_i/A_{i+n})$. Temperature scans were accomplished in a temperature range from room temperature to 650°C with heating and cooling cycles under secondary vacuum at a rate of 2 K/m. The initial strain amplitude was $1 \cdot 10^{-4}$ and the logarithmic decrement was estimated from 30 oscillations. Amplitude-dependent internal friction scans were performed before and after thermal treatments to induce precipitation. Free-decaying oscillations were measured at room temperature (T_{ROOM}) as a function of the applied strain in the range from $2 \cdot 10^{-5}$ to $1 \cdot 10^{-3}$ counting 60 oscillations. The precipitation treatment was made in-situ at 550°C for 2 hours. The maximum amplitude of the strain, corresponding to the first oscillation ($n=1$), is reported as x-coordinate on the plot (Fig. 2). Tests with 40 oscillations were also made in order to check if internal friction level changed. Internal friction was always measured both by the Yoshida method applied to the fast Fourier transform (FFT) [9] and by measuring directly the logarithmic decrement on all oscillations. No discrepancy between the methods was observed seeing that the difference in internal friction between the methods does not exceed $5 \cdot 10^{-6}$. The points that are plotted are those obtained from the FFT.

Seebeck coefficient or thermoelectric power is the magnitude of an induced thermoelectric voltage in response to a temperature gradient across a material. TEP was measured at T_{ROOM} under a temperature difference of 20°C using the apparatus described in [10]. In metallic alloys, this parameter, related with the diffusion of electrons, is strongly influenced by the presence of solute atoms, dislocations and the nature of secondary phases. Therefore, TEP provides an accurate technique to investigate the microstructure evolution of alloys taking place during various phase transformations such as precipitation [7]. AR and ST samples were sequentially annealed at increasing temperatures ranging from 250°C to 900°C. Each heat treatment was followed by water quenching to freeze the structure at the last temperature of annealing and TEP was finally measured at room temperature. Two measurement sets were carried out with heat treatment time

of 20 minutes and 2 hours. Each measurement took about two minutes to get a stationary temperature profile within the sample.

Further indications about mechanical properties were obtained by hardness testing. Vickers hardness was measured on AR, ST and CW samples underwent to the same heat treatment described for TEP experiments. After each treatment, the surface of the samples was accurately prepared for indentation by mechanical polishing and at least ten indentations were obtained for each temperature treatment using a 0.300 kg load and a loading time of 30 seconds. By measuring the diagonal length d of the indentation, hardness value was calculated as $H_V = F/A \approx (1.8544 \cdot F)/d^2$, where F is the load expressed in kg force and A is the surface area of the indentation in mm^2 [8].

3. Results

In the present paper, the effects of precipitation hardening in Co-Ni-Cr alloy on dissipative motion of dislocations by amplitude-dependent internal friction measurements are investigated. The evolution of the microstructure during various thermal treatments is studied by thermoelectric power, hardness tests and internal friction measurements. A variation in the chemical composition of the matrix due to depletion of alloying elements in solid solution is associated with precipitation and leads to an improvement of mechanical properties.

Precipitation was originally revealed by the TEP spectra carried out on both CW and ST samples and characterized by the presence of a maximum at around 600°C (see Fig. 1a). TEP is highly sensitive to the presence of solute atoms and precipitation induces a depletion of atoms from solid solution, which results in an increase in the Seebeck coefficient. The dissolution of such precipitates brings back elements into the matrix as can be observed by the reduction of the TEP value [7]. As previously noted, the TEP measurements were made at room temperature on specimens that had been annealed at increasing temperatures up to 900°C and cooled by water quenching after each annealing. The lower start level for CW sample is due to a higher density of dislocations introduced by deformation reducing the TEP value [11] while their restoration tends to increase it and after the treatment at 500°C the CW curve reaches the ST one.

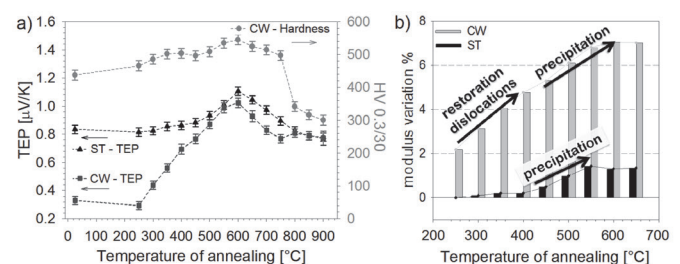


Fig. 1. (a) TEP and hardness after annealing of 20 min and (b) variation of the elastic modulus at T_{ROOM} with temperature after isochronal heat treatments of 20 min

Micro-indentation hardness test shows a hardness increase at the same temperature as the maximum in TEP curve

in agreement with the hypothesis of precipitation hardening (Fig. 1a). The drop of hardness after annealing at 750°C is due to recrystallization in accordance with the Hall-Petch relation as supported also by internal friction investigations and optical metallography images (not shown). Similarly to measurements made by TEP, samples were heat treated at different temperatures during 20 minutes and their room temperature modulus was measured (Fig. 1b). It is noticed that the cold-worked sample modulus already increases with treatments above 200°C. Both in the CW sample and ST sample the modulus increase above 400°C could be attributed to the precipitation evidenced by TEP.

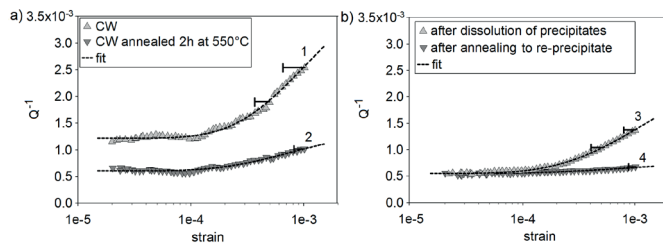


Fig. 2. ADIF curves at T_{ROOM} for different thermally treated specimens before and after precipitation. a) Cold-worked material (curve 1) annealed 2h at 550°C (curve 2); b) cold-worked specimen annealed 2h at 650°C to dissolve the precipitates formed at 550°C (curve 3) and then annealed again 2h at 550°C (curve 4). Curves fitted according to Eq. (2) are plotted in dashed lines and the maximal variations of the amplitude on the counted oscillations are reported

Figure 2 shows the results of the ADIF measurements made on a cold-worked (CW) sample after various thermo-mechanical treatments. The plots refer to a sample measured just after cold-work (curve 1), after a first annealing of 2h at 550°C to produce precipitation (curve 2), after a further treatment at 650°C to dissolve precipitates (curve 3), and finally after a second annealing at 550°C to reproduce precipitation (curve 4). Since the experiments have been made in free decay oscillations mode, the maximum decrease of the strain amplitude on the counted oscillations is assimilated to an error bar on the strain axis. The curves obtained in the absence of precipitates are characterized by a certain critical strain above which the damping rises rapidly with the maximum strain amplitude applied because of the onset of dislocations mechanism [6] as discussed in the next section. The low strain internal friction horizontal line is the amplitude independent component. Notice that we did not assess the intrinsic damping of the pendulum that should be of the order of magnitude of $2 \cdot 10^{-4}$. For a qualitative interpretation of the damping rise this is not crucial. Heat treatments on laminated material provides a general lowering of the damping level explainable by restoration of dislocations as suggested already by the difference on dynamic modulus variations taken at room temperature after isochronal heat treatments at increasing temperature on CW and ST specimens (Fig. 1b).

By comparing the curves 1-3 with 2-4 in Fig. 2, we note that as consequence of the annealing period providing precipitation, the dependence of damping on strain amplitude is strongly reduced. In fact, both the curves 2 and 4, obtained after precipitation, show an extended region where the internal

friction is independent on the strain amplitude and a weaker increase once the dislocation breakaway is activated. The slightly wavy form of curve 1 in Fig. 2a is not believed as due to an essential behavior. It should be considered within the usual scatter of measurements even if some trend might appear to the reader. The superposition at low strain amplitude of the curves 3 and 4 in Fig. 2b can be explained by the fact that the internal friction background at first approximation depends on the total amount of dislocations, which should be similar for the curves 3 and 4 after dislocation restoration.

4. Discussion

According to the results presented in the previous section, thermal treatments performed in the temperature range from 400°C to 600°C lead to the formation of precipitates able to hinder dislocations motion affecting significantly the mechanical properties of the material and increasing its strength. As a matter of fact, the maximum on TEP curves (see Fig. 1a) can be interpreted as due to a precipitation with depletion of alloying elements from solid solution resulting in an increase of Seebeck coefficient. The dissolution at temperature higher than 600°C changes again the chemical composition of the matrix bringing back the elements in solution and lowering the TEP value [7]. Moreover, the reproducibility of the TEP curve over a double sequence of isochronal thermal treatments performed on a same sample (not reported here) suggests that a precipitation-dissolution process occurs. Such precipitation phenomenon is supported by the hardness experiments, showing an increase of the hardness at the same temperature as the maximum in TEP curve.

The influence of such precipitates on the mechanical properties is also evidenced in Fig. 1b where the relative variation of the dynamic modulus at room temperature after isochronal heat treatments of 20 min at increasing temperature is plotted for both CW and ST samples. The dynamic modulus exhibits an increase after annealing performed in the temperature range from 400°C to 600°C. On CW sample, such increase is preceded by a further increase, taking place at lower temperature, and explainable by the restoration of excess dislocations introduced by cold-work [12].

ADIF results shown in Fig. 2 can also be interpreted by supposing precipitation and considering pinning-depinning of dislocations. By comparing the curves 1-2 with 2-4 in Fig. 2, we note that the annealing causing the precipitation, strongly changes the dependence of damping capacity on the strain amplitude. The curves 1 and 3, obtained in absence of precipitates, show a rapid rise of the damping with the maximum strain amplitude applied as a consequence of the dislocation breakaway from weak pinning points. After 2 hours of annealing at 550°C leading to precipitation, dislocation motion is hindered by such precipitates acting as strong pinning points and the internal friction remains almost flat (see curves 2 and 4 in Fig. 2).

The Köhler-Granato-Lücke model can be used as a base for a semi-quantitative assessment of the microstructure parameters [13]. The motion of a dislocation under an oscillating stress can be considered to be analogous to the motion of a vibrating string and the energy dissipated is linked

with the length of dislocation segment that undergoes vibration [14]. The length of loops is supposed to be determined at first by the intersections of dislocation network, therefore there are two characteristic lengths to be considered: L_N the distance between strong pinning points and L_{PD} determined by weak pinners. For very small stress, the loops between weak pinning points (L_{PD}) bow out reversibly. The bowed loops exert a net force on the pinning points, tending to overcome the binding force, with a certain maximum value F_B . When the force applied through dislocation loop on the pinning points is greater than the binding force, a breakaway from one pinning point occurs and the whole segment is catastrophically torn away from the row of weak pinners as shown in Fig. 3a.

The mechanical loss caused by dislocation segments involved in such a mechanism can be calculated using the relationship [13,15]:

$$\phi = \phi_i + (\rho L_N^3 / 6 L_{PD}) \cdot (F_B / b E L_{PD}) \cdot (1 / \varepsilon_0) \cdot \exp[-(F_B / b E L_{PD}) \cdot (1 / \varepsilon_0)], \quad (1)$$

where ϕ_i is the background given by the damping independent on amplitude, ρ is the density of dislocations participating in the breakaway process, L_N is the mean length of dislocation segments between strong pinners and L_{PD} is the mean distance between weak pinners, F_B is the binding force between a dislocation and a weak pinning point, b is the modulus of the Burgers vector, E is the unrelaxed modulus, ε_0 is the strain amplitude. Since the composition of specimens is the same, the parameters in Eq. (1) except L_N and L_{PD} can be treated as constants.

To fit the experimental ADIF curves we rewrite Eq. (1) in simpler way:

$$y = y_0 + A \cdot (B/x^\alpha) \cdot \exp[-(B/x^\alpha)] \quad \text{with } A \sim \rho L_N^3 / L_{PD} \text{ and } B \sim 1 / L_{PD}, \quad (2)$$

where α is a phenomenological parameter taking into account that the strain of the specimen in a torsional pendulum is not uniform [16].

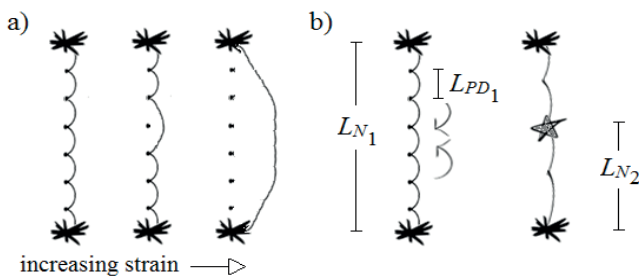


Fig. 3. a) Breakaway mechanism; b) sketched effect of aging process on the characteristic lengths

By comparing the parameters obtained from the different ADIF curves, we can deduce the effect of heat treatments on L_N and L_{PD} . As shown in Table 1, the aging process at 550°C causes a reduction of L_N according to the formation of widespread strong pinning points. The weak pinning entities involved in the breakaway process could be alloying elements placed in substitutional or interstitial position creating a stress field with which dislocations interact. This hypothesis is supported by the

fact that, as consequence of the depletion of solute atoms from solid solution to form precipitates, a simultaneous increase of L_{PD} and a reduction of the mean number of weak pinners $n = L_N / L_{PD}$ are found. Obviously, strong pinners should be small precipitates.

TABLE 1

The formation of finely dispersed precipitates acting as strong pinning points reduces L_N and simultaneously increases L_{PD}

Variation of characteristic lengths of "pinning model" as consequence of aging process:	$L_{N2} = 0.5 L_{N1}$
	$L_{PD2} = 1.2 L_{PD1}$
$n_2 = 0.4 n_1$	

Preliminary images obtained by transmission electron microscopy (TEM) from the ST sample annealed 2h at 550°C (not shown) indicate that these precipitates are coherent with the matrix and very finely dispersed. Their size is only few nanometers similar to Guinier-Preston zones and the average distance of this precipitates, corresponding to L_N , can be estimated in about 40 nm. Further TEM investigations are necessary to confirm this observation and the nature of these precipitates.

5. Conclusions

In this work, the effect of precipitation hardening mechanism on the dislocation motion by amplitude-dependent internal friction measurements was studied. TEP and hardness test were performed as complementary techniques. A model applied on ADIF spectra provides an interpretation of the modifications in the characteristic lengths of dislocations.

Hardness tests confirm that the main hardening of the material comes from strain hardening, but a secondary hardening may occur by aging the material in the temperature range from 400°C to 600°C leading to precipitation. The precipitation process is evidenced by TEP indicating a depletion of solute atoms with a maximum between 550°C and 600°C depending on the annealing time. Above such temperature, TEP variation suggests a re-resolution of the precipitates.

Mechanical spectroscopy measurements carried out as a function of temperature show a continuous change of the dynamic modulus that can be attributed to changes in the microstructure. Dislocations recovery after cold-work occurs at 150°C and it is evidenced by a decrease in internal friction. Above this temperature, a further increase of elastic modulus is related to dislocation pinning by precipitates. A qualitative analysis of the amplitude-dependent internal friction spectra was carried out by using a phenomenological model based on Granato-Lücke theory providing an interpretation of the modifications in the characteristic lengths of dislocations, which suggests that annealing leads to the formation of strong pinning points identifiable with the mentioned precipitates.

Consistently with all our experimental results, we can speculate that aging the material at a temperature between 400°C and 600°C creates finely dispersed precipitates with a size of a few nanometer acting as strong pinning points on dislocations.

As a result, they hinder dislocation motion providing an increase in the yield strength of the material, being responsible for the secondary hardening of this super-alloy.

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