RŮST ZRN V TECHNICKÉM NIKLU
GRAIN GROWTH IN TECHNICAL NICKEL

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Abstrakt
U technického niklu (99.5%) válcovaného za studena byly studovány kinetické a termodynamické parametry růstu zrn a vývoj dvojčat během žíhání v argonu při teplotách 600–1100 °C. Aktivační energie růstu zrn 285.5 kJ/mol, stanovená v teplotním intervalu 900–1100 °C, potvrzuje proces řízený objemovou difúzi. Výsledky jsou srovnány s daty získanými po žíhání na vzduchu a je diskutován pravděpodobný vliv oxidace na růst žíhacích dvojčat.

Abstract
In the cold-rolled commercially pure nickel (99.5%), the kinetic and thermodynamic parameters describing the grain growth and evolution of twins during annealing in argon at 600–1100 °C has been studied. In the temperature range 900–1100 °C, the activation energy for grain growth was found to be 285.5 kJ/mol, which indicates the bulk diffusion controlled process. The results were compared to the literature data obtained after annealing in air. A possible influence of oxidation on grain growth and formation of annealing twins in commercial nickel is discussed.

1. INTRODUCTION
The lifetime of metallic materials exposed to thermo-mechanical loading is strongly influenced by their microstructure (strictly speaking by defects in a perfect crystal lattice), such as grain size, shape of grains, grain boundary type and texture. In 1984, Watanabe [1] introduced the concept of grain boundary (GB) design, widely known as grain boundary engineering (GBE), in which material properties could be enhanced by controlling the grain boundary character distribution (GBCD) via thermo-mechanical processing (TMP). Till this time, the science underlying the TMP schedules used in grain boundary engineering is surprisingly poorly understood [2], and most of the processing schedules, some of which are patented, are purely empirical.

In order to establish a bit of theoretical background for controlling the GBCD, there is a need for systematic research to clarify how and why recrystallization and grain growth (GG) affects the number and distribution of special boundaries. It is also the intent of the present work to monitor the evolution of GBCD during recrystallization and grain growth in the commercial purity nickel as a representative of the wide range of nickel-based industrial alloys.

As has already been published 50 years ago [3], some requirements must be fulfilled for grain growth kinetics studies to be successful:

• The metal should be free from inclusions and dispersed phases
Recrystallization must not take place
The smallest specimen dimension should not be smaller than about ten times the mean grain diameter
Grain-counts should be made not directly on the surface as the growth behavior of the surface grains is not representative

Another objective of the present work is to propose an additional requirement taking into account an influence of the environment.

Finally, even if quite a number of papers are concerned with grain growth, twin evolution and corrosion of nickel and nickel-based alloys, it should be noted that only limited work has been done to understand the relationship between these phenomena.

1.1 Grain growth
The problem of grain growth in polycrystalline materials is one of the oldest and most investigated in physical metallurgy. The thermodynamic driving force for grain growth is the reduction in excess energy of a polycrystalline sample with respect to single crystal that results in total grain boundary area reduction and thereby in increasing the average grain size.

There are several methods to determine the kinetic and thermodynamic characteristics of grain growth. Accordingly to the mostly used practice and the commonly observed parabolic grain growth, a time dependence of grain size \( d \) at respective temperature can be expressed as

\[
d^2 - d_0^2 = k t,
\]

where \( d_0 \) is the initial grain size, \( k \) is the kinetic constant and \( t \) is the anneal time. A set of measurements of \( k \) at different temperatures \( T \) provides the Arrhenius type equation

\[
k = k_0 \exp(-E / RT),
\]

where \( k_0 \) is the constant, \( E \) is the activation energy of grain growth and \( R \) is the universal gas constant. By comparing \( E \) with activation energy of the various diffusion processes, on can determine the major process controlling grain growth. Eqs. (1) and (2) can be integrated into

\[
d^2 - d_0^2 = k_t \exp(-E / RT).
\]

1.2 Grain boundary character distribution
A wide variety of required chemical and/or physical properties of commercial alloys can be achieved by suitable modification of the GBCD through thermo-mechanical processing. With regards to the prediction of susceptibility to inter-granular cracking, much recent work has shown that the connectivity of random GBs is the more reliable criterion than the originally proposed total frequency of special CSL boundaries [1].

The connectivity of random GBs can be quantitatively evaluated using both the triple junction distribution [4] and/or the random boundary cluster length [5]. An increase in the frequency of resistant 2-CSL and 3-CSL triple junctions (that are composed of two or three special boundaries) can enhance corrosion resistance of polycrystalline materials even if the grain boundary character distribution is the same [6].

The relative fraction of twin variants (\( \Sigma 3^n \Sigma 3, n>1 \)) has recently been considered [7] as an additional criterion related to the connectivity of random GBs. The twin variants (mainly \( \Sigma 9 \) and \( \Sigma 27 \)) form in process of twin-twin interactions during GB migration and contribute to disrupting the random GB network. On the contrary, low ratio of \( \Sigma 3^n / \Sigma 3 \) indicates the presence of twins predominantly within the grains and GB connectivity persists. Also according to this approach, neutral-twin boundaries that do not yield other low-\( \Sigma \) CSL
boundaries (e.g. twin variants) along neighboring interfaces have no effect on random boundary connectivity, and must therefore be discounted from the total special boundary fraction if the depth of inter-granular attack is to be accurately predicted. Assuming Σ9 GBs and Σ27 GBs in the microstructure arise solely from twin interactions then the number of effective Σ3 GBs from which these variants originate can be estimated [7] as

\[
f_{\Sigma3}^{\text{eff}} = -\frac{f_{\Sigma27} + f_{\Sigma9}}{2} + \left(\frac{f_{\Sigma27} + f_{\Sigma9}}{2}\right)^2 - 2\left(f_{\Sigma3}f_{\Sigma29} + f_{\Sigma3}f_{\Sigma27} - f_{\Sigma27} - f_{\Sigma29}\right)^{1/2}. \tag{4}
\]

As promised in the recently published review [8], it is of future significance to investigate the formation mechanism as well as the migration behavior of all types of Σ3 boundaries.

2. EXPERIMENTAL

2.1 Sample preparation

The coin-shaped samples were spark cut (diameter 10mm) from the 99.5% cold-rolled nickel foil 2 mm thick. One flat surface of each specimen was ground on silicon carbide laps, then polished successively on diamond paste laps to a 1 µm finish and finally cleaned in an ultrasonic bath filled in turn with ethanol, acetone and chloroform (p. a. purity grade). Subsequently, the specimens were wrapped in tantalum foil and then encapsulated in argon filled quartz tubes prior to the heat treatment at temperatures 600–1100 °C. The annealed samples were found to be bright and shiny and showed a well-defined microstructure as a result of thermal etching. Mostly, the direct EBSD measurement was possible. If not, an electrolytic etching was applied in order to remove the surface layer.

2.2 Grain growth

In this work, a straightforward evaluation of activation energy \( E \) of grain growth by means of Eq. (3) was used, while the time dependences following Eq. (1) are too time-consuming. In

![Fig. 1. Dependence of time \( t_{\text{max}} \) of grain growth on temperature in pure (4N) and technical purity (2N3) nickel (data taken from [9]).](image)

<table>
<thead>
<tr>
<th>annealing temperature [°C]</th>
<th>( t ) [ks]</th>
<th>( t_{\text{max}} ) [ks]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>10.8</td>
<td>22.6</td>
</tr>
<tr>
<td>1000</td>
<td>10.8</td>
<td>151</td>
</tr>
<tr>
<td>900</td>
<td>10.8</td>
<td>1 500</td>
</tr>
<tr>
<td>800</td>
<td>93.6</td>
<td>25 319</td>
</tr>
<tr>
<td>700</td>
<td>500.4</td>
<td>–</td>
</tr>
<tr>
<td>600</td>
<td>669.6</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 1. Annealing conditions; data for the GG time \( t_{\text{max}} \) taken from [9] or, in case of temperatures 1100 and 800 °C, extrapolated from plot in Fig. 1.
this case, though, keeping the annealing time well below the time \( t_{\text{max}} \), during which grain growth occurs, is very important. To estimate the suitable annealing conditions, the literature data published in [9] on the dependence of \( t_{\text{max}} \) on temperature in technical purity (2N3) nickel were used, smoothed and extrapolated to other temperatures (see Fig. 1 and Table 1) in this paper. Simultaneously, the corresponding values for pure nickel (4N) taken also from [9] are presented in Fig. 1.

2.3 GBCD

For evaluation of the grain boundary character distribution, a Jeol JSM 6460 scanning electron microscope with Oxford Instruments Inca Crystal EBSD analyzer was used. The obtained data were further analyzed in terms of the CSL model. All detected boundaries were categorized as follows: (i) low angle boundaries \((4.8^\circ \leq \text{angle} \leq 10^\circ)\), often referred to as \(\Sigma 1\) type boundaries), (ii) CSL boundaries \((3 \leq \Sigma \leq 29)\), (iii) frequently occurred twin boundaries with \(\Sigma=3\) as a special case or, if none of these, as (iv) random boundaries. From the grain size evaluation by means of standard software, all special GBs were excluded.

3. RESULTS AND DISCUSSION

Using Eq. (3) and values presented in Table 2 at temperatures 900–1100 °C, a combined thermodynamic/kinetic expression for grain growth in 99.5% nickel was derived

\[
d^2 - d_0^2 = 0.6966t \exp(-285.5kJ mol^{-1}/RT) \ [m^2].
\]

In the process of evaluation, we found for initial grain size \(d_0\) a very plausible value \(d_0 = 12 \mu m\). This quantity well corresponds to the values 10 and 12 \(\mu m\) at temperatures 700 and 800 °C, respectively, that seems to be a result of complete recrystallization during annealing (no grain growth so far). This process is clearly presented in Fig. 2: a large amount of added work in cold-rolled samples leads to the grain size decrease from \(d_0 = 36 \mu m\) in as-received sample to \(d = 19, 10\) and \(12 \mu m\) after anneal at 600, 700 and 800 °C, respectively. As the temperature rises, the parabolic grain growth begins and Eq. 3 can be successfully applied (see Fig. 3).

Table 2. Measured data of grain size and GBCD and calculated fraction of effective \(\Sigma 3\) GBs

<table>
<thead>
<tr>
<th>annealing temperature [°C]</th>
<th>(t) [ks]</th>
<th>(d) [µm]</th>
<th>(\Sigma 1)</th>
<th>(\Sigma 3)</th>
<th>(\Sigma 9)</th>
<th>(\Sigma 27)</th>
<th>random</th>
<th>effective (\Sigma 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>10.8</td>
<td>322</td>
<td>0.7</td>
<td>51.7</td>
<td>0.9</td>
<td>0.7</td>
<td>45.4</td>
<td>17.0</td>
</tr>
<tr>
<td>1000</td>
<td>10.8</td>
<td>121</td>
<td>1.5</td>
<td>52.5</td>
<td>2.0</td>
<td>0.7</td>
<td>42.5</td>
<td>21.8</td>
</tr>
<tr>
<td>900</td>
<td>10.8</td>
<td>40</td>
<td>0.9</td>
<td>32.9</td>
<td>3.5</td>
<td>0.9</td>
<td>58.5</td>
<td>15.1</td>
</tr>
<tr>
<td>800</td>
<td>93.6</td>
<td>12</td>
<td>0.6</td>
<td>46.2</td>
<td>4.9</td>
<td>1.4</td>
<td>45.4</td>
<td>32.4</td>
</tr>
<tr>
<td>700</td>
<td>500.4</td>
<td>10</td>
<td>0.7</td>
<td>37.1</td>
<td>4.4</td>
<td>1.1</td>
<td>54.0</td>
<td>30.4</td>
</tr>
<tr>
<td>600</td>
<td>669.6</td>
<td>19</td>
<td>0.5</td>
<td>57.8</td>
<td>7.3</td>
<td>2.8</td>
<td>31.0</td>
<td>40.1</td>
</tr>
<tr>
<td>as-received</td>
<td>0</td>
<td>36</td>
<td>3.9</td>
<td>32.8</td>
<td>3.0</td>
<td>1.2</td>
<td>59.3</td>
<td>26.4</td>
</tr>
</tbody>
</table>
Fig. 2. Dependence of the grain size on annealing temperature (for the annealing parameters, see Table 1) in commercial purity nickel.

The estimated activation energy of the grain growth \(E = 285.5 \text{ kJ mol}^{-1}\) well corresponds to the activation energy for volume self-diffusion in nickel (280–290 kJ mol\(^{-1}\), for summary see [10]). This result agrees also with the grain growth activation energy published in [9] for 2N3 nickel (283.7 kJ mol\(^{-1}\)). In contrast to this, a value \(E = 143.5 \text{ kJ mol}^{-1}\) was presented in [9] for 4N nickel, which indicates more likely the grain boundary diffusion controlled process.

Fig. 3. Thermodynamic relationship describing the grain growth in commercial purity nickel in comparison with literature data [11].

Fig. 4. Dependence of the fraction of \(\Sigma 3s\) on reciprocal temperature in commercial purity Ni after anneals in argon (this work) and air [11].

Fig. 5. Microstructure of commercial purity Ni in as-received state (\(\Sigma 1, \Sigma 3\) and remaining boundaries in green, blue and yellow, respectively).
As it is seen from Figs. 2 and 3 and Eq. (5), conventional grain growth kinetics was observed following annealing in argon from 600 to 1100 °C in the case of the nickel samples measured in this work. After recrystallization (600–700 °C), grain size increases slowly initially (800 °C), than increases rapidly approaching a parabolic growth rate (900 –1100 °C). This behavior can be roughly represented by a $J$-shaped curve.

Fig. 6. Microstructure of commercial purity nickel after anneals at various temperatures ($\Sigma 1$, $\Sigma 3$ and remaining boundaries in green, blue and yellow, respectively).
Fig. 3 shows also the comparison of our data with the analogous measurements related to grain growth in commercially pure nickel (99.5%) annealed for 6 h in air [11]. However, contrary to our results, the growth follows a sigmoid (S-shaped) curve that can be divided into three stages. The first is slow initial growth (825–900 °C) and once this is finished, a period of rapid growth follows (925–1000 °C). Finally, subsequent growth is limited by several factors (1000–1050 °C) and grain size even gently decreases. It is worthy to note that the curve looks linear in the middle part (about 950 °C) and, in this part, follows approximately Arrhenius dependence of GG recalculated from our data using Eq. (5) and $t = 6$ h (dashed line in Fig. 3). However, at higher temperatures, grain growth in nickel annealed in air [11] is probably impeded by some obstacles, such as particles or voids resulting from interaction with ambient air [12].

Fig. 4 shows dependence of the fraction of the Σ3 GBs on reciprocal temperature in commercial purity nickel after anneals in argon (this work) and air [11]. At temperatures above 800 °C, both curves behave qualitatively similarly, though a higher number of Σ3s is detected in the former case. In this case also, influence of environment could be perhaps a reason for mentioned difference.

Additionally, the fraction of the effective Σ3 GBs (calculated from Eq. 4 using data presented in Table 2) in commercially pure nickel annealed in argon is demonstrated in Fig. 4. At temperatures above 850 °C, about 20% of the effective Σ3s was present, unlike of 30–40% of those at low temperatures (600–800 °C). It should be noted, that low $f_{\Sigma 3}^\text{eff}$ at high temperatures corresponds well with results of Randle et al. [11]. In all samples measured, she refers to a presence of low fraction (1–2%) of Σ9 boundaries along with high portion of Σ3s whereas no other CSL boundaries were observed. Thus, a fraction of the effective Σ3s is assumed to be low, newly created are predominantly annealing twins within grains and, in consequence, random boundary network continues unbroken. This finding agrees with design of two methods of thermo-mechanical processing (TMP) reported in the literature (for summary see [6]).

One approach has been to deform the material to small strain levels about 5%, followed by annealing at temperatures low enough to prevent recrystallization. This method is commercially impractical in that it requires very time consuming anneals (10–15 h). Moreover, it leads to the undesirable grain growth due to the long annealing times. The second approach is based on a multi-cycle treatment of higher strain levels (above 10%) with anneals at high temperatures (950–1050 °C) where very short times (2–10 min) are used.

In regards to this work, our experiments at low temperatures provide a high fraction of the effective Σ3s. This is not surprising since the anneal conditions correspond to the requirements of the first method of TMP. On the other hand, our treatment at high temperatures (3 h) yields a substantially lower fraction of the effective Σ3 boundaries, even thought a proportion of all Σ3s remains relatively high. This result is in agreement with the literature where the authors recommend short times to impede grain growth and together to reach a high number of Σ3s.

**CONCLUSIONS**

Kinetic and thermodynamic parameters describing the grain growth during annealing at 600–1100 °C has been studied in the cold-rolled nickel of technical purity (99.5%).

In the temperature range 900–1100 °C, a combined thermodynamic/kinetic expression was derived

$$d^2 - d_0^2 = 0.6966t \exp(-285.5kJ mol^{-1} / RT) \ [m^2].$$
The activation energy value suggests that grain growth in nickel is controlled by bulk diffusion.

A considerable number of annealing twins together with low portion of the effective $\Sigma 3$ variants ($\Sigma 9s$, $\Sigma 27s$) were detected at high annealing temperatures and relatively long times. By contrast, at lower temperatures, high portion of the effective boundaries was found as a result of frequently occurred twin-twin interactions indicated by enhancement of the density of $\Sigma 3$ variants.

After annealing in argon atmosphere, parabolic grain growth kinetics has been observed in this work as contrasted to impeded grain growth due to annealing in air published in the literature.

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