Grain growth and grain size effects on the thermal expansion properties of an electrodeposited Fe–Ni invar alloy

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The effects of grain growth and size on the thermal expansion behavior of an electrodeposited Fe–Ni invar alloy have been studied. The results showed a method of achieving different thermal expansion coefficients over a wide range of 3.1–7.8 × 10⁻⁶ K⁻¹ for the same alloy through grain size control. The thermal expansion difference between grain boundaries and crystallites was enlarged in the invar alloy. The nanocrystalline samples exhibited moderate thermal stability up to 623 K and then abrupt grain growth, with a contraction in volume.

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The thermal expansion behavior of nanocrystalline (NC) materials has been proven to be quite different from conventional polycrystalline materials, both theoretically [1,2] and experimentally [3–8]. Described as two-component systems made up of nanocrystallites and grain boundaries (or interfaces) with a non-negligible volume fraction, NC materials should exhibit an increasing thermal expansion coefficient (CTE) with decreasing mean grain size, as a result of the extra volume of the grain boundaries. Klum et al. [9] measured the CTE of the interface directly and found that it was apparently larger than that of the crystalline state. Birringer [3] found that the CTE of a NC Cu sample was nearly twice that of Cu single crystals. Measurements by Lu and Sui [4] showed that CTE increased markedly with a reduction in the average grain size of as crystallized NC Ni-P samples. Although there exist some inconsistent experimental results [10–12], the relationship between CTE and grain size provides a possible way to control the thermal expansion behavior of NC materials, which is attractive in terms of practical application, if the thermal stability causes no problems.

In this study, we prepared an invar composition Fe–Ni alloy (37 ± 2 wt.% Ni, detected by inductively coupled plasma mass spectrometry, ICP) through electrodeposition. Conventional polycrystalline Fe–Ni alloys with a nickel composition of about 36% are well known as invar alloys, from their unique low CTE values near zero as a result of the so-called ‘invar effect’ [13,14]. It would be interesting to see how their NC counterparts perform – for example, whether the grain boundaries display an ‘invar effect’ or not and whether the CTE values are low for the crystallites but not the grain boundaries. If the CTE values were very low for the crystallites but not for the grain boundaries the thermal behavior of the NC material should be more sensitive to grain size, such that a wide range of CTEs could be obtained just through the control of grain size.

The Fe–Ni alloy sample with the thickness of over 1 mm was prepared through direct current electrodeposition, which has been demonstrated to be an effective technique for producing porosity-free metals [15]. The detailed chemical composition of the electrolyte is listed in Table 1. Electrodeposition was carried out at 313 ± 1 K, a cathode current density of 3.7 A dm⁻² and a stirring rate of 200 rpm. An iron–nickel sheet (50 wt.% nickel) was used as the anode and a copper plate as the cathode [16]. After deposition the Fe–Ni alloy plate was removed from the substrate by electric spark cutting and then cut into pieces of the desired size for subsequent heat treatment and characterization. Differential scanning calorimetry (DSC) (Netzsch 404) and in situ X-ray diffraction (XRD) (Rigaku DMAX/2550)
studies were performed on the as deposited sample to observe grain growth during the heating process. Two DSC scans were performed: (1) the sample was heated from ambient to 850 K at a rate of 10 K min\(^{-1}\); (2) the sample was cooled after the first scan, then the heating run repeated, to obtain a baseline. In situ XRD measurements were performed with Cu K\(\alpha\) radiation (\(\lambda_{\text{Cu}} = 1.54056 \, \text{Å} \)) at 40 kV and 250 mA. The sample was placed on a platinum sample stage and then put into the oven chamber, which was evacuated using a mechanical vacuum pump to avoid oxidation. Both temperature measurement and calibration were performed with thermoelectric couples (PtRh13\%/Pt). A heating rate of 5 K min\(^{-1}\) was used with annealed Si powders as the reference sample. The whole process was carried out in an argon atmosphere. The accuracy of the elongation measurements was about 1.25 \times 10^{-6} \, \text{m}. Thin film samples for transmission electron microscopy (TEM) were prepared by iron thinning and a JEOL 2100 microscope was used for grain size observation with an acceleration voltage of 200 keV.

The DSC results are shown in Figure 1A. A heat release peak was observed in the first scan but not in the second, indicating an irreversible exothermic reaction from 635 to 669 K. From XRD observation of the (1 1 1) peak at different temperatures, as shown in Figure 1B, almost the same level of broadening below 648 K was observed, indicating limited grain growth below that temperature. However, abrupt grain growth from about 16 to 30 nm occurred between 623 and 648 K, as estimated by Scherer formula after instrumental broadening was subtracted. The DSC and XRD results show that the electrodeposited NC alloy did not grow significantly until above 623 K. Similar results have been reported for electrodeposited Ni [17,18] and Co [19], but no evident heat release of ‘nucleation’ was observed in our DSC study. The thermal stability of NC materials at a certain temperature has been demonstrated [20] and the phenomenon of abrupt grain growth has been observed in many materials [17,19,21].

Annealing of the as deposited samples was performed below and above the onset temperature of abrupt grain growth, and a reference sample with a mean grain size of about 10 \(\mu\)m was also prepared. The details are shown in Table 2. Figure 2 shows bright field TEM images summarizing the grain size evolution of the NC Fe–Ni alloy after isochronal annealing. Samples A and B consisted of ultrafine (on the nanometer scale) crystallites. Compared with sample A, the grain size in sample B had increased only slightly. In sample C, annealed above the temperature where abrupt grain growth happens, the grains had grown to submicron scale. The as deposited sample consisted of pure fcc structure (γ-phase) as indicated by electron diffraction patterns. No phase transformation happened after annealing, as observed from qualitative XRD analyses (results not shown).

Figure 3 shows the strain changes during continuous heating for the different grained samples. The slope changes may result from thermal expansion or/and microstructure evolution. Based on the slope change of the curves the temperature range can be divided to four zones, as shown in Figure 3.

Below about 380 K, in zone a, the curves show an approximate linear relation of strain with increasing temperature, which means within the temperature range the CTE remained almost constant for the samples: 7.87 \times 10^{-6} \, K^{-1} for sample A, 7.28 \times 10^{-6} \, K^{-1} for sample B, 5.12 \times 10^{-6} \, K^{-1} for sample C and 3.13 \times 10^{-6} \, K^{-1} for sample D. The CTE decreased markedly with an increase in the initial mean grain size, ranging from about 3 \times 10^{-6} to 8 \times 10^{-6} \, K^{-1}, which suggests a method of achieving different CTEs for the same alloy merely through grain size control. This would appear feasible in terms of practical application.
For example, matching the thermal expansion of ceramics such as Al₂O₃ and SiC with the equivalent metallic alloy could be realized with. In zone b the curve for sample A exhibits a shallow slope compared with that in section a. From the in situ XRD results it can be seen that this phenomenon does not result from abrupt grain growth. This possibly results from a reduction in excess free volume in the specimen due to the relaxation of defects or microstrain [8] during ‘nucleation’ [17,18], although nucleation heat release was not observed by DSC. In zone c the curves for both sample A and sample B show a deep trough from 623 to 673 K, reaching the deepest point at about 648 K, indicating a contraction in length, which is fully consistent with the temperature range where abrupt grain growth happens, as revealed by DSC and in situ XRD. A reduction in excess free volume occurs in materials during grain growth, causing densification of the material, and it has been shown that the atomic density at nanocrystalline boundaries is lower than that of the perfect crystal by 10–30% [1,22]. NC samples A and B underwent pronounced grain growth in this temperature range and an obvious volume contraction was revealed by the strain curves. Similar phenomena were also observed in NC Ni–P [4] and Se [5].

Table 2. Annealing details and the mean grain sizes of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat treatment</th>
<th>Mean grain size</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>As deposited</td>
<td>12.5 nm</td>
</tr>
<tr>
<td>B</td>
<td>Annealed at 523 K for 12 h, cooled in oven</td>
<td>14.7 nm</td>
</tr>
<tr>
<td>C</td>
<td>Annealed at 673 K for 12 h, cooled in oven</td>
<td>~0.4 μm</td>
</tr>
<tr>
<td>D</td>
<td>Annealed at 953 K for 12 h, cooled in oven</td>
<td>~10 μm</td>
</tr>
</tbody>
</table>

The grain sizes were estimated from TEM bright field observations (samples A–C) or optical microscope observation (sample D).

Figure 2. TEM micrographs showing the microstructure of the samples. (A) As deposited and after annealing for 12 h at (B) 523 K and (C) 673 K. (A-1) Electron diffraction pattern of sample A.

Figure 3. Curves of strain versus temperature during thermal expansion for samples with different initial grain sizes.
Crystallites, respectively.

As a appropriate scaling of the boundaries contribution as:

\[ a_{\text{NC}} = F_B a_B + (1 - F_B) a_C \]  

where \( F_B \) is the volume fraction of grain boundaries and \( a_B \) and \( a_C \) are the CTEs of the grain boundaries and the crystallites, respectively.

From a simple geometric reckoning, \( F_B \) is estimated as \( \delta/d \), where \( \delta \) is a constant dependent on the interface thickness [1]. Thus, we get:

\[ a = a_{\text{NC}} - a_C = (a_B - a_C) \delta/d \]  

CTE data used for the calculation are determined from the slope in the temperature range ~300–380 K, with no evident microstructural change in this temperature region, and the value of sample D was taken as the approximate value for the crystallite. The grain size data are shown in Table 2. A plot of \( \Delta a/a_C \) versus \( 1/d \) for the samples of different grain size is shown in Figure 4. The curve shape demonstrates that the CTE difference between grain boundaries and crystallites varies with grain size, and shows decreasing CTE with decreasing grain size. A similar result was reported by Lu and Sui for NC Ni–P samples [4], but the values of \( \Delta a/a_C \) observed in this study are close to 150% for the NC samples, much higher than those of Lu and Sui, which were below 60%. The large value of \( \Delta a/a_C \) implies a greater thermal expansion difference between grain boundaries and crystallites in the Fe–Ni invar alloy. Although the mechanism is not yet known, this is convincing evidence that the ‘invar effect’ exists in the Fe–Ni crystallites, resulting in very low CTE in conventional polycrystalline alloys [13,23]. While, as deduced from the thermal expansion behavior of samples with different grain sizes, it seems no such ‘invar effect’ exists in the grain boundaries.

In summary, the electrodeposited NC invar alloy exhibits moderate grain size stability and, because the ‘invar effect’ affects only crystallites and not grain boundaries, the thermal expansion difference between them is quite large and grain size plays a significant role in the total thermal expansion properties, which provides a promising way to achieve a wide range of CTE values in invar alloys of the same composition.

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Figure 4. A plot of \( \Delta a/a_C \) versus \( 1/d \) of samples with different grain sizes.

For samples C and D, annealed above the temperature range at which abrupt grain growth occurs, no such contraction was apparent.

To estimate the contribution of grain boundaries to the total CTE a simple model proposed by Wagner [1] was used to simplify the NC materials as two-component systems with nanocrystallites and grain boundaries. Then the CTE of the NC material can be estimated by appropriate scaling of the boundaries contribution as:

\[ a_{\text{NC}} = F_B a_B + (1 - F_B) a_C \]  

where \( F_B \) is the volume fraction of grain boundaries and \( a_B \) and \( a_C \) are the CTEs of the grain boundaries and the crystallites, respectively.

From a simple geometric reckoning, \( F_B \) is estimated as \( \delta/d \), where \( \delta \) is a constant dependent on the interface thickness [1]. Thus, we get:

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References:

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