Diffusion of chromium in nanocrystalline iron produced by means of surface mechanical attrition treatment

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Abstract

By means of surface mechanical attrition treatment (SMAT) to a pure iron plate, a nanometer-grained surface layer without porosity and contamination was fabricated. The average grain size in the top surface layer (of 5 µm thick) is about 10–25 nm, and the grain size stability can be maintained up to 653 K. Cr diffusion kinetics in the nanocrystalline Fe phase was measured by using second ion mass spectrometry within a temperature range of 573–653 K. Experimental results showed that diffusivity of Cr in the nanocrystalline Fe is 7–9 orders of magnitude higher than that in Fe lattice and 4–5 orders of magnitude higher than that in the grain boundaries (GBs) of α-Fe. The activation energy for Cr diffusion in the Fe nanophase is comparable to that of the GB diffusion, but the pre-exponential factor is much higher. The enhanced diffusivity of Cr may originate from a large volume fraction of non-equilibrium GBs and a considerable amount of triple junctions in the present nanocrystalline Fe sample processed by means of the SMAT technique.

Keywords: Nanocrystalline; Surface mechanical attrition treatment; Thermal stability; Diffusion; Grain boundary

1. Introduction

Nanocrystalline materials are structurally characterized by ultrafine grains and a large number of grain boundaries (GBs). These defective GBs may act as “short-circuit” diffusion channels, so that atomic diffusion in nanocrystalline materials is expected to be much enhanced relative to their coarse-grained polycrystalline counterparts. This point has been supported by the experimental results as reported in the literature [1–8]. Measurements of the self-diffusion in nanocrystalline Cu with a grain size of about 8 nm (produced by means of inert gas condensation and consolidation) [1] showed that the activation energy for diffusion is 0.64 eV, comparable to that for surface diffusion, being only 1/3 of the lattice diffusion. The diffusivities are found to be about 16 orders of magnitude larger than the lattice values. Kolobov et al. [5] noticed that GB diffusivities of Cu in a nanocrystalline Ni (with a grain size of about 300 nm, synthesized by means of severe plastic deformation) are about 4–5 orders of
magnitude higher than those in the coarse-grained Ni. Mütschele and Kirchheim [4] compared the diffusion of hydrogen in a consolidated nanocrystalline Pd (with an average grain size of 5 nm) with that in a Pd single crystal in a large range of H concentration. They found that the diffusion coefficient in the nanocrystalline Pd is several times of the lattice diffusivity at higher H concentrations. Enhanced atomic diffusivities were also detected in the intermetallic-amorphous nanocomposites relative to the amorphous alloy, due to the presence of numerous amounts of nanocrystallites [7].

Nevertheless, understanding of the nature of atomic diffusion in nanocrystalline materials is still far away. So far, experimental measurement data on atomic diffusion in nanocrystalline materials are still very limiting and scattering. Most of the previous experimental studies were performed on consolidated nanocrystalline samples from ultrafine powders [1–4], in which nanometer-sized porosities as well as gaseous contaminations could not be avoided. Diffusion kinetics will be significantly influenced by these processing artifacts. For the nanocrystalline samples made by means of severe plastic deformation [5,6], grain sizes are usually large (around 100 nm or above) and high density of lattice (and GB) dislocations are created in the synthesis processing. The grain size effect in the nanometer region on the diffusion properties could not be clearly identified from these samples in which the volume fraction of GB is small and the lattice dislocation effect might be evidently included.

Thereby, in order to investigate the nanocrystallite effect on atomic diffusion kinetics, porosity-free and contamination-free nanocrystalline pure metal samples are needed, in which grain sizes should be small enough in order to exclude other effects. A recently developed technique, surface mechanical attrition treatment (SMAT) [9,10], seems to be appropriate for this purpose. SMAT enables the fabrication of a surface layer with a mean grain size of about 10 nm on various metals [11–15]. The nanocrystalline layer is free of contamination and porosity because the nanocrystallization process is induced by the severe plastic deformation at very high strain rates [10]. In this work, we produced a layer of nanocrystalline Fe (with grain sizes of 10–25 nm) on a pure Fe plate by means of SMAT technique. With this porosity-free and contamination-free nanocrystalline Fe layer, the diffusion behaviors of Cr in the nanocrystalline Fe phase are studied in comparison to those in the coarse-grained polycrystalline Fe.

2. Experimental

2.1. Sample preparation

An iron plate (7 mm by 100 mm by 100 mm in size) with a purity of 99.95 wt% was subjected to the SMAT processing in order to achieve a nanostructured surface layer. Prior to the treatment, the Fe sample was annealed at 1223 K for 120 min in a vacuum furnace to eliminate the effect of mechanical polishing on the surface structure and to obtain homogeneous coarse grains of α-Fe phase (~100 µm).

During the SMAT procedures, hardened steel balls (with a mirror-like surface and a diameter of 8 mm) were placed at the bottom of a cylinder-shaped vacuum chamber attached to a vibration generator, with which the balls were resonated and impacting multi-directionally onto the sample surface to be treated at the upper side of the chamber. The experimental setup and the details of SMAT processing were described in [10,11]. Because of the high vibration frequency of the system, the sample surface was impacted repetitively by a large number of balls within a short period of time. As a consequence, the sample surface is plastically deformed with a high strain rate and grains in the surface layer are expected to be effectively refined. After the SMAT (with a vibration frequency of 50 Hz and a duration of 60 min), the surface roughness is comparable to that of the original sample.

2.2. Structure characterization

The structural evolution of the surface layer of the Fe sample was studied by X-ray diffraction (XRD) analysis using a Rigaku D/max 2400 X-ray diffractometer (12 kW), with Cu Kα radiation. Small angular steps of 2θ = 0.02° were taken to measure the intensity of each Bragg diffraction
peak. The counting time of 20 s was used to exactly measure the width of diffraction peak in the step-scanning mode. The average grain size and the mean microstrain of the nanocrystalline Fe were derived from the line broadening of bcc Fe (1 1 0), (2 0 0), (2 1 1), (2 2 0), (3 1 0) and (2 2 2) Bragg diffraction peaks, by using the Scherrer and Wilson method [16].

Meanwhile, microstructure features of the nanocrystalline layer were examined in a Philip EM-420 transmission electron microscope (TEM) at a voltage of 100 kV. Thin foil samples for TEM observations were cut by electro-spark discharge technique, grinded, dimpled and finally ion-thinned at low temperatures.

2.3. Composition analysis

Cr concentration profiles in samples after diffusion annealing treatments were determined by using secondary ion mass spectrometry (SIMS) [17,18] on a Cameca IMS 6F analyzer. During sputter-sectioning, the primary ion beam of O$_{2}^+$ (15.0 kV, 2.0 µA and 0.10 mm in diameter) was rastered over an area of 0.3 × 0.3 mm$^2$, and at an appropriate time interval the primary O$_{2}^+$ beam was stopped at the center of the square to measure the intensities of secondary ions (Cr$^+$ and Fe$^+$) by a mass spectrometer. The results obtained by the preliminary experiments showed that the intensity of Cr$^+$ to the intensity sum of Cr$^+$ and Fe$^+$, i.e., $I_{Cr}/(I_{Cr} + I_{Fe})$, varied proportionally to concentration of Cr. Hence, the ratio of $I_{Cr}/(I_{Cr} + I_{Fe})$ was used as the Cr concentration ($C_{Cr}$) in this work. Because of the similar bond strengths of Cr and Fe, it is reasonable to assume that the sputtering rate keeps a constant during the course of sputtering. The depth was calculated from the sputtering time scale and the mean sputtering rate, which was determined by the total sputtering time and the total depth of the SIMS crater measured using an alpha-step 200 instrument (with an accuracy of 0.1 µm).

3. Results and discussion

3.1. Microstructure characterization of the SMAT Fe

Detailed microstructural characterization of the surface layer in the as-treated Fe sample by means of XRD analysis and TEM observations, together with an underlying nanocrystallization mechanism during SMAT in terms of the severe plastic deformation mode of bulk materials [19,20], can be found in [11]. Fig. 1(a) shows the average grain size as a function of depth determined from the XRD and TEM experiments, respectively. It is clear that the surface layer is nanostructured and the grain size increases gradually with an increment of depth. In the top layer of 5 µm thick, the grain sizes are in the range of 10–25 nm. The nanometer-sized grains are equiaxed with random crystallographic orientations, as indicated in the typical plane view TEM observation of the top surface layer and its corresponding selected area electron diffraction (SAED) pattern (Fig. 1(b)). Differences in the resultant grain sizes determined from TEM and XRD may originate from the fact that the XRD analysis averages the structure information of a much thicker layer (about 5 µm) than TEM (less than 0.5 µm).

Positron annihilation spectroscopy measurements of the surface layer were performed to determine the processing-induced porosities. The intensity of the long-lifetime component of positron, indicative of nanometer-sized pores [21,22], was found to be negligible (about 0.6%) for the as-treated sample. This result, much differing from that for the consolidated nanocrystalline samples (usually more than 10% [22]), implies no residual porosity existing in the nanocrystalline surface layer. Microscopy observations verified that no porosity is visible in the SMAT Fe sample (see Fig. 1(b) and [11]). The compositional analysis by using the energy disperse spectrum (EDS) showed that the contaminations in the as-treated surface layer are negligible (below the measurement resolution).
3.2. Thermal stability of the nanostructured surface layer

In order to determine the experimental conditions (temperature and time) for diffusion of Cr in the nanocrystalline Fe phase, thermal stability of the nanocrystalline phase against grain growth was measured. The average grain size and the mean microstrain were determined by using XRD analyses and TEM observations for the SMAT specimens annealed at various temperatures in a vacuum furnace (heated at 10 K/min to the annealing temperature, holding for 3 min before cooling down to ambient temperature). Fig. 2 shows variations of the average grain size and the mean microstrain in the top surface layer (about 5 µm thick) with the annealing temperature derived from XRD analysis. The microstrain drops gradually to zero at about 623 K, accompanied by a structure relaxation. A significant increment in grain size onsets at about 773 K, below which a slight increase of grain size was noticed, from 12 nm in the as-treated sample to about 21 nm at 773 K. This result was verified by TEM observation. When the sample was annealed at 823 K, an obvious abnormal grain growth occurs, resulting in the formation of rather large grains (>100 nm in size,
e.g. marked “A” in Fig. 3) co-existing with small ones (marked “B”), a typical configuration of recrystallization.

The isothermal experiments were carried out by heating the as-treated specimen to 573, 613 and 653 K and holding for 1440, 600 and 120 min, respectively. Fig. 4 shows TEM images for the sample annealed at 653 K for 120 min, from which almost an identical microstructure was seen as in the as-treated sample. The mean grain size is about 8 nm. Measured grain sizes of the top surface layer after the isothermal annealing treatments by using TEM and XRD analysis were listed in Table 1 and

Fig. 3. A typical plane view TEM observation of the top surface layer in the SMAT Fe sample heated to 823 K (at a heating rate of 10 K/min and holding for 3 min). Grains with very different sizes are labeled “A” and “B”.

Fig. 4. (a) Bright-field and (b) dark-field TEM images showing plane view microstructures in the top surface layer of the SMAT Fe sample annealed at 653 K for 120 min. Inserts in (a) and (b) are its corresponding SAED pattern and a statistic distribution of grain size derived from the dark-field TEM images, respectively.
Table 1
The average grain size and the mean microstrain of the top surface layer in the SMAT Fe samples annealed at different temperatures determined from XRD analyses and TEM observations

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Annealing temperature (K)</th>
<th>Annealing duration (min)</th>
<th>XRD</th>
<th>TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Grain size (nm)</td>
<td>Microstrain (%)</td>
</tr>
<tr>
<td>I</td>
<td>As-treated</td>
<td>/</td>
<td>12</td>
<td>0.12</td>
</tr>
<tr>
<td>A</td>
<td>573</td>
<td>1440</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>613</td>
<td>600</td>
<td>18</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>653</td>
<td>120</td>
<td>18</td>
<td>0</td>
</tr>
</tbody>
</table>

plotted in Fig. 2. It shows that no evident grain growth of the nanocrystalline Fe occurs when the sample is isothermally annealed below 653 K.

3.3. Determination of diffusion coefficient

Experimental results shown above demonstrated that a nanocrystalline Fe layer with grain sizes of 10–25 nm was fabricated by means of the SMAT technique, in which porosity and contamination were not detected. The grain size stability in the nanocrystalline Fe layer can be maintained up to at least 653 K. Such a sample is suitable for an investigation of diffusion properties below the destabilization temperature.

The SMAT sample surface was cleaned and electroplated with a layer of pure chromium (about 4 µm thick). The electroplating process was carried out at 343 K with a current of 0.27 A/cm² in an agitated solution of 25.0 wt% CrO₃, 2.50 wt% H₂SO₄ and H₂O. Fig. 5 shows a cross-sectional TEM view of the interface between the electroplated Cr layer and the nanocrystalline Fe. The Cr layer bonds closely with the surface of the nanocrystalline layer without any gap or void between them. The long direction of Cr columnar grains is perpendicular to the interface. SAED patterns of the Cr layer indicated the grains are bcc-structured with an apparent texture. The energy disperse spectrum (EDS) analysis showed that the as-electroplated Cr layer has a purity higher than 99.98 at.%. The Fe–Cr couple sample was isothermally annealed for diffusion at 573 K for 1440 min (sample A), 613 K for 600 min (sample B) and 653 K for 120 min (sample C), respectively. For comparison, the original coarse-grained Fe sample with an electroplated Cr layer was annealed at 653 K for 120 min (sample D) and 1113 K for 60 min (sample E), respectively. XRD profiles indicated only α-Fe and Cr solid solutions in the samples after the diffusion treatments.

The Cr concentration profiles determined by using SIMS for the SMAT and the reference samples after different diffusion treatments are shown in Fig. 6. The Cr concentration in the reference sample D (treated under the same diffusion condition with sample C) decreases sharply to zero within a depth of about 0.5 µm. However, for sample A, B and C, Cr concentration profiles extend to
a much larger depth, indicative of much enhanced diffusivities of Cr in the nanocrystalline Fe layer under the same diffusion circumstances.

Measurement of grain size stability as presented in the last section indicated that the grain size and the microstrain of nanocrystalline Fe in the surface layer vary slightly during the diffusion treatment. The diffusion properties of Cr in the Fe–Cr system weakly depend upon the Cr concentration [23]. So it is reasonable to assume that the diffusion coefficient of Cr in the nanocrystalline surface layer \((D_n)\) is a constant during the corresponding diffusion treatment. While the diffusion in the coarse-grained Cr layer should be slower than Cr diffusion in nanocrystalline Fe (as shown in Fig. 6), the exact solution of diffusion equation by using different mathematic treatments is not critical for evaluation of the diffusion coefficient [24]. For simplification, one may have the following equation according to Fick’s second law of diffusion:

\[
\frac{\partial C}{\partial t} = D_n \frac{\partial^2 C}{\partial x^2}
\]

with boundary conditions:

\[
\begin{align*}
\text{when } t &= 0, & C &= 1, & x &> 0 \\
& & C &= 0, & x &< 0
\end{align*}
\]

and

\[
\begin{align*}
\text{when } t &> 0, & C &= 1, & x &= -\infty \\
& & C &= 0, & x &= \infty
\end{align*}
\]

Application of these conditions to Eq. (1) yields a solution

\[
C = \frac{1}{2} [1 - \text{erf}(u)]
\]

with

\[
u = x/2\sqrt{D_n t}
\]

where \(C\) represents the Cr concentration at a depth \(x\) after diffusion treatment time \(t\) (the origin of \(x\) is defined as the position where the measured Cr concentration is 50%). The expression \(\text{erf}(u)\) is the Gaussian error function.

\(C\) values are obtained from the Cr concentration profiles as in Fig. 6. From Eq. (2), one may get the values of \(\text{erf}(u)\) at depth \(x\) after corresponding diffusion treatments, and then derive the values of \(u\) following the tabulation of Gaussian error function values [25]. Relationships between \(u\) and \(x\) for sample A, B, C (within a thickness of about 2 \(\mu\)m close to the origin in the nanocrystalline Fe) and sample D are plotted in Fig. 7 (sample E was not included because of its different boundary conditions and the resultant solution of Eq. (1)). The data points in the Cr layer were excluded in the plots because of slow diffusion kinetics in the coarse-grained Cr layer and the presence of possible oxide, adlayer [18] between the electroplated Cr and the SMAT Fe surface. The data at a larger depth (>2 \(\mu\)m) for each sample were also excluded due to the accumulated effect of the varied diffusion properties (with an increasing grain size) in the nanocrystalline Fe surface layer. The diffusion of Cr in the nanocrystalline Fe layer within a thickness of about 2 \(\mu\)m, in which the grain size can be considered as a constant (about 10 nm), is expected to be in a steady state.

According to Eq. (3), a linear relation should be derived in the plot of \(u\) vs \(x\) in this steady state diffusion region as shown in Fig. 7, the slope \(G\) of the fitting lines can be expressed as
Fig. 7. Plots of $u$ vs $x$ for various samples after diffusion treatments as indicated ($u$ is a function of depth, i.e. $x/\sqrt{D_t}$).

$$G = \frac{1}{2}\sqrt{D_n t}$$ (4)

A good agreement between the fitting straight lines and the data points, as in Fig. 7, supports the validity of the simplified diffusion model as in Eq. (1). $D_n$ is then determined from slopes of the fitting lines, as listed in Table 2. Similarly, diffusion coefficients of Cr in the reference (coarse-grained) Fe samples ($D_c$) were also obtained. The value of $D_c$ at 653 K derived from this experiment is rather close to that of the GB diffusivity [26]. This might be attributed to the fact that it was determined from the very thin top surface layer (less than 0.2 µm) and a relatively large error is associated due to the limited data points.

Assuming that the diffusion kinetics follows the Arrhenius dependence in the concerned temperature range, one may see that Cr diffusivities in the nanocrystalline Fe within the temperature range of 573–653 K are 7–9 orders of magnitude higher than those in the Fe lattice and 4–5 orders of magnitude larger than those in the α-Fe GBs, as calculated according to the literature data [26,27] (see Table 2). The activation energy of Cr diffusion in the nanocrystalline Fe ($Q_n$) was calculated from the temperature dependence of $D_n$, as shown in Fig. 8, in comparison with those for the Fe lattice diffusion [27], the lattice diffusion in the bcc Fe–Cr alloy [23] and the GB diffusion of α-Fe [26]. The obtained value of $Q_n$, being $197 \pm 21$ kJ/mol, is evidently smaller than that for the lattice diffusion ($Q_v = 241$ kJ/mol), but comparable to that for the Cr diffusion in α-Fe GBs ($Q_b = 218$ kJ/mol). The pre-exponential factor $D_n0$ is about 14 m$^2$/s, which is much higher than those for the lattice diffusion ($D_v0 = 2.5 \times 10^{-2}$ m$^2$/s) and the GB diffusivity ($D_b0 = 6.0 \times 10^{-2}$ m$^2$/s), evaluated from the reported values in the literature [26] assuming the width of GB $\delta = 1$ nm) of Cr in α-Fe.

### 3.4. Diffusion mechanisms

The measured results showed comparable activation energies for the Cr diffusion in the nanocrystalline Fe and for that in α-Fe GBs, implying that Cr diffusion along GBs is a dominating mechanism.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>NC iron ($D_n$) (m$^2$/s)</th>
<th>CG iron ($D_c$) (m$^2$/s)</th>
<th>Lattice ($D_v$) (m$^2$/s)$^a$</th>
<th>GB ($D_b$)(m$^2$/s)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>573</td>
<td>$1.7 \times 10^{-17}$</td>
<td></td>
<td>$1.2 \times 10^{-26}$</td>
<td>$8.6 \times 10^{-22}$</td>
</tr>
<tr>
<td>613</td>
<td>$1.6 \times 10^{-16}$</td>
<td></td>
<td>$3.7 \times 10^{-25}$</td>
<td>$1.7 \times 10^{-20}$</td>
</tr>
<tr>
<td>653</td>
<td>$2.8 \times 10^{-15}$</td>
<td>$3.6 \times 10^{-19}$</td>
<td>$7.6 \times 10^{-24}$</td>
<td>$2.3 \times 10^{-19}$</td>
</tr>
<tr>
<td>1113</td>
<td></td>
<td>$2.2 \times 10^{-15}$</td>
<td>$1.5 \times 10^{-15}$</td>
<td>$3.5 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

$^a$ Calculated from the diffusion equation given by Bowen et al. [27].

$^b$ Calculated from the diffusion equation given by Kaur et al. [26].
Fig. 8. Temperature dependence of the diffusion coefficients of Cr in the nanocrystalline (NC) and the coarse-grained (CG) Fe, in comparison with those for the α-Fe lattice diffusion [27], the α-Fe GB diffusion [26] and the diffusion in Fe–Cr alloy [23].

in the nanocrystalline α-Fe phase. The ultrafine-grained structure provides a considerable volume fraction of GBs, roughly about 30 vol.% for an average grain size of 10 nm [28], which may serve as numerous fast diffusion “channels” for Cr. The much enhanced diffusivity of Cr in the nanocrystalline Fe sample relative to that in the coarse-grained Fe is another straightforward evidence for the diffusion kinetics dominated by the fast GB diffusion.

It is interesting to note that the measured diffusivity of Cr in the nanocrystalline Fe is apparently larger than the diffusivity along GBs in the coarse-grained Fe, as calculated according to the literature data [26] (see Table 2). This might be attributed to the microstructure characteristics of the nanocrystalline Fe sample processed by means of the SMAT technique.

During the SMAT processing of the pure Fe plate, severe plastic deformation at high strain rates, estimated to be about $10^{2-3}$ s$^{-1}$, takes place in the surface layer. It leads to the formation of an extremely high density of dislocations that act as precursors for new GBs subdividing the original coarse grains [10,11]. Repetitive multi-directional straining causes progressive grain refinement into the nanometer scale and formation of dislocations either in the refined grains or associated with the large amount of GBs. Eventually, nanometer-sized α-Fe grains were formed with a high density of GB dislocations in the top surface layer, as reflected from the large mean microstrain $(\langle \varepsilon^2 \rangle^{1/2}=0.12\%$) determined by means of XRD analysis, while the density of lattice dislocations was negligible, as evidenced by the high-resolution electron microscopy observations [11]. Actually, when grain sizes are smaller than a critical value, dislocations will hardly pile up in grains and the nanometer-sized crystallites become dislocation free [29]. The GBs formed via severe plastic deformation are usually in non-equilibrium states [5,19] that are associated with a higher stored energy or a higher density of defects compared to the equilibrium GBs in conventional coarse-grained materials. Or, in other words, the non-equilibrium GBs in the present nanocrystalline Fe sample possess a higher Gibbs free energy than the conventional GBs, that may facilitate Cr diffusion along GBs by decreasing the defect formation energy [12,30].

In addition, with a decrease of grain size, the volume fraction of triple junctions (i.e. the intersection pipes of three adjoining crystals) drastically increases as well. When the grain size is reduced to 10 nm, the amount of triple junctions can be as high as a few volume percents [28]. The existence of plenty of triple junctions in the nanocrystalline surface layer has been demonstrated by the results of positron annihilation spectroscopy measurements. The intensity of the intermediate–lifetime component of positron, indicative of intersections of different crystallite interfaces [22], was found to be about 11.6% in the top surface layer of the as-treated sample. Because triple junctions structurally possess a larger excess volume compared to GBs, the Cr diffusion along them will be much facilitated. In the nanocrystalline Fe surface layer, both the non-equilibrium GBs and the triple junctions might contribute to the much enhanced diffusivity of Cr.

The enhanced diffusivity of Cr in the nanocrystalline Fe sample is another straightforward evidence for the diffusion kinetics dominated by the fast GB diffusion.
talline Fe can be further interpreted by using a GB diffusion model of defect migration. It is known from computer simulation studies and experimental measurements that GB diffusion in α-Fe is dominated by vacancy mechanism [31,32]. The energy of vacancy formation in GBs is smaller than that in the lattice and decreases with the GB energy [30]. For the nanocrystalline Fe produced by means of SMAT, the high Gibbs free energy of GBs and triple junctions will make vacancy formation much easier than that in the conventional GBs. Furthermore, the binding energy of vacancies to GBs also decreases with an increasing GB free energy [31]. So the diffusivity of Cr in the nanocrystalline Fe will be much improved compared with that along GBs in the coarse-grained Fe. At the same time, the interstitial migration might also contribute to the much-enhanced diffusivity of Cr in the nanocrystalline Fe because the interstitial formation energy is comparable with the vacancy formation energy in the high-energy GBs and triple junctions [30,32].

4. Summary

A nanocrystalline α-Fe surface layer free of porosity and contamination was fabricated on a pure iron plate by means of the SMAT technique. The average grain size in the top surface layer of 5 μm thick is about 10–25 nm. Diffusivities of Cr in the nanocrystalline Fe layer within the temperature range of 573–653 K are 7–9 orders of magnitude higher than those in the Fe lattice and 4–5 orders of magnitude higher than in the α-Fe GBs. The measured activation energy for Cr diffusion in the nanocrystalline Fe is comparable to that of the GB diffusion, but the pre-exponential factor is much higher. The enhanced diffusivity of Cr in the nanocrystalline Fe can be attributed to a large volume fraction of non-equilibrium GBs with a high density of dislocations and a considerable amount of triple junctions in the present nanocrystalline Fe sample.

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