Effect of rare earth Ce on martensite structure of Fe–Mn damping alloy

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Abstract

This work mainly studied the effect of rare earth Ce on the martensite structure of Fe–Mn alloy. According to thermodynamic and two-dimensional mismatch theories, the phase and morphology of the Fe–Mn alloy were characterized through x-ray diffraction and scanning electron microscopy. Results show that rare earth oxides and sulfides, such as CeS, CeO2S, and Ce2O3, are easily formed after Ce is added to the alloy. The order of formation is generally CeS, CeO2S, and Ce2O3. Ce2O2S and Ce2O3 can become nucleation cores of gamma austenite, and the nucleation core of Ce2O3 is the most effective. The addition of Ce to the alloy evidently refines the quenched structure, increases the nucleation core of austenite, and increases the driving force of martensitic transformation, thereby increasing the number of lath martensite lamellae and reducing the thickness. The thickness of lath martensite lamellae is approximately 1–2 μm, and most of them are triangular.

1. Introduction

With the increasing power and frequency of modern machinery, vibration and noise have seriously affected the fatigue resistance, stability, and environmental adaptability of equipment and reduced the performance and life of equipment [1–4]. Nearly 80% of accidents and equipment damages in machine manufacturing industry are caused by vibration shock, and the noise generated by vibration reduces the concealment and combat effectiveness of military equipment [5–7]. Therefore, the ability of vibration and noise reduction of a machinery should be improved. Damping materials can irreversibly convert the absorbed mechanical energy into heat energy or other forms of energy through an internal mechanism and further consume it, generating internal friction [8, 9]. Damping materials show broad application prospects, such as submarine propellers, brake discs, shield machines, gears, and crushers.

Five kinds of damping alloys, namely, twin crystal alloys (Mn–Cu and Ni–Ti) [10], ferromagnetic alloys (Fe–Cr, Fe–Al) [11], multiple phase alloys (gray cast iron, Zn–Al) [12], dislocation alloys (Mg–Zr) [13], and Fe–Mn alloy [14, 15], are formed according to different damping mechanisms. Fe–Mn alloys are suitable to be used in parts with large vibration and impact because of their good damping properties, high strength, and low cost [16]. Therefore, researchers have been exploring the damping properties of Fe–Mn alloys since the late 1970s. However, research progress on how to improve the damping properties of alloys is slow. Appropriate rare earth elements can reduce the stacking faults of shape memory alloys and facilitate the formation of lath martensite [17–19]. For example, the addition of Ce restricts grain growth, refines austenite grain, enlarges the interface area of a crystal phase, and increases the driving force of martensitic transformation. Thermodynamic analysis and two-dimensional mismatch theory are used to calculate the formation conditions and sequence of rare earth Ce oxides, oxygen sulfides, and sulfides in Fe–Mn alloys and to determine whether they can be used as the nucleation core of γ–Fe heterogeneous nucleation.

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2. Experimental materials and methods

Experimental alloys were melted in a medium-frequency induction furnace with industrial pure iron and electrolytic manganese as raw materials. After homogenizing and annealing were performed at 1150°C for 24 h, an ingot (Ф30 mm × 300 mm) was machined into a round rod at the initial and final forging temperatures of 1050°C and 850°C, respectively. After heat treatment was administered, bars were processed into cubes with an edge length of 10 mm so that they could be characterized through SEM and XRD. The chemical composition and heat treatment process of the alloy are shown in table 1.

After inlaying, grinding, polishing, and corrosion in 1.2% K2S2O5 aqueous solution, the microstructures of the alloy specimens were observed using a ZEISS-SUPRA55 scanning electron microscope. The phase composition of the alloy was determined with a Philips x-ray diffractometer. The target material, tube pressure, and flow rate were Cu Kα, 40 kV, and 50 mA, respectively.

3. Results and discussion

3.1. Thermodynamic calculation

After Ce was added to the alloy, the conditions and sequence of the formation of oxides and sulfides in the alloy were analyzed by comparing the Gibbs free energy of the obtained products. The amount of Ce in molten steel was set at 1 mol, and the probability of interaction between each element and Ce was equal. The basic thermodynamic data of the main oxides and sulfides in the alloys are shown in table 2.

The interaction coefficients of the elements in the alloy are calculated in the classical Wagner form as shown in formula (3.1):

\[ \log f_i = \sum_{j=1}^{n} e_{ij}[\text{mass}\%j], \]  

(3.1)

where \( f_i \), \( e_{ij} \), and \([\text{mass}\%j]\) are the activity coefficient of elements, the interaction coefficient between elements, and the mass percentage of elements, respectively. The activity of each element in the alloy can be calculated using formula (3.2).

\[ a_i = f_i[\text{mass}\%i] \]  

(3.2)

The activity interaction coefficients \( e_{ij} \) of the elements in the alloys are shown in table 3.

The activity of each element in the alloy can be calculated by using Formulas (3.1) and (3.2) as shown in table 4.

\[ [\text{Ce}] + 3[O] = \text{Ce}_2O_3(s) \quad \Delta G^0 = -715560 + 180T \]

Using formula (3.3), we can obtain that \( \Delta G = -4.52 \times 10^4 \approx 0 \). Adding Ce to the alloy can spontaneously form \( \text{Ce}_2O_3 \). Similarly, \( \text{CeS} \) and \( \text{CeO}_2S \) can be formed by adding Ce to the alloy.

| Table 1. Chemical composition and heat treatment of Fe–Mn alloy. |
|----------------|---------|---------|---------|---------|---------|
| Alloys         | Mn      | S       | O       | Si      | Ce      | Fe      | Heat treatment process            |
| Fe–15Mn        | 15.320  | 0.020   | 0.101   | 0.130   | 0.000   | balanced | 1050°C × 1 h Water cooling        |
| Fe–18Mn        | 18.100  | 0.027   | 0.015   | 0.100   | 0.000   | Balanced |                                |
| Fe–18Mn–0.23Ce | 18.300  | 0.014   | 0.007   | 0.070   | 0.023   | Balanced |                                |

| Table 2. Basic thermodynamic data of compounds in alloys [18, 20] (1873 K). |
|----------------|------------------|------------------|
| deoxidation desulfurization reaction | Standard Gibbs free energy J mol⁻¹ | Product solubility product reaction | Equilibrium constant (solubility product) K |
| \([\text{Ce}] + 3[O] = \text{Ce}_2O_3(s)\) | \(\Delta G^0 = -715560 + 180T\) | \(\text{Ce}_2O_3(s) = 2[\text{Ce}] + 3[O]\) | \(K_2 = 3 \times 10^{-21}\) |
| \([\text{Ce}] + [S] = \text{CeS}(s)\) | \(\Delta G^0 = -1224740 + 390T\) | \(\text{CeS}(s) = [\text{Ce}] + [S]\) | \(K_3 = 4.8 \times 10^{-6}\) |
| \([\text{Mn}] + [S] = \text{MnS}(s)\) | \(\Delta G^0 = -163146 + 91T\) | \(\text{MnS}(s) = [\text{Mn}] + [S]\) | \(K_4 = 1 \times 10^{-2}\) |
| \(2[\text{Ce}] + [S] + 2[O] = \text{CeO}_2S_2(s)\) | \(\Delta G^0 = -1366460 + 364T\) | \(\text{CeO}_2S_2(s) = [\text{Ce}] + [S] + 2[O]\) | \(K_5 = 1.3 \times 10^{-20}\) |

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In general order of formation is presented as follows: CeS, CeO2S, and Ce2O3. However, under the same conditions, MnS cannot be generated. In order to calculate the activity of elements in alloys, the following formula can be used:

$$\text{Activity interaction coefficient of elements in alloys } \sum$$

$$T = 1873 \text{ K}$$

| Activity coefficient $f_i$ | Activity $a_i$ |
|---------------------------|----------------|
| $f_{\text{Mn}}$ | $a_{\text{Mn}}$ |
| $f_{\text{Ce}}$ | $a_{\text{Ce}}$ |
| $f_{\text{O}}$ | $a_{\text{O}}$ |
| $f_{\text{S}}$ | $a_{\text{S}}$ |

$$3.34 \times 10^{-1} \quad 8.95 \times 10^{-1} \quad 8.95 \times 10^{-1} \quad 4.72 \times 10^{-1} \quad 6.11 \quad 2.06 \times 10^{-2} \quad 6.27 \times 10^{-3} \quad 6.61 \times 10^{-3}$$

**Table 4. Activities of elements in alloys after Ce is added.**

| Activity coefficient $f_i$ | Activity $a_i$ |
|---------------------------|----------------|
| $f_{\text{Mn}}$ | $a_{\text{Mn}}$ |
| $f_{\text{Ce}}$ | $a_{\text{Ce}}$ |
| $f_{\text{O}}$ | $a_{\text{O}}$ |
| $f_{\text{S}}$ | $a_{\text{S}}$ |

| Matching interface | (0001)Ce2O3 ||| (110)γ–Fe | (0001)Ce2O3 ||| (110)γ–Fe | (0001)Ce2O3 ||| (111)γ–Fe |
|--------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| (hkl) Ce2O3       | [120]          | [110]          | [110]          | [110]          | [110]          | [110]          |
| (hkl) γ–Fe        | [010]          | [011]          | [100]          | [110]          | [011]          | [110]          |
| $d_{\text{Ce2O3}}$ | 3.926          | 6.780          | 3.926          | 3.928          | 3.928          | 3.928          |
| $d_{\gamma–Fe}$   | 3.732          | 4.173          | 3.732          | 3.735          | 3.735          | 3.737          |
| $\gamma$         | 0              | 11.56          | 15             | 0              | 0              | 0              |
| $d_{\text{Ce2O3}} \cdot \cos \theta$ | 3.926 | 6.642 | 3.928 | 6.775 | 3.402 | 3.928 | 6.804 | 3.928 |
| $\delta_{(hkl)} \cdot \gamma–Fe$ | 14.50 | 12.80 | 5.17 |

**Table 5. Lattice parameters of substrates and nucleated phases.**

| Element/\(\text{nm}\) | Ce2O3 | γ–Fe | CeS | Ce2O2S |
|------------------------|-------|------|-----|--------|
| Lattice parameters     | 0.3889| 0.3681| 0.5790| 0.4000 |
| Crystal structure      | hcp   | fcc  | NaCl| hcp    |

**Table 6. Lattice mismatch calculations of Ce oxides and γ–Fe.**

3.2. Theoretical calculation of two-dimensional mismatch degree

Spatial two-dimensional mismatch can be used to analyze the nucleation particle validity [21]. We can determine the compound that can become the nucleation particle of γ–Fe by calculating the validity of Ce2O3, Ce2O2S, and CeS to the heterogeneously nucleated particle of γ–Fe. Two-dimensional lattice mismatch can be expressed by using the following formula:

$$\delta_{(hkl)} = \sum_{i=1}^{3} \left| d_{(iuvw), hkl} \cdot \cos \theta - d_{(iuvw), hkl} \right| \times \frac{1}{3} \times \frac{100}{\%}$$

$$\cos \theta = \frac{u_1 u_2 + v_1 v_2 + w_1 w_2}{\sqrt{(u_1^2 + v_1^2 + w_1^2)(u_2^2 + v_2^2 + w_2^2)}}$$

In Formulas (3.4) and (3.5), (hkl), is a low surface index of the base, (uvw), is a low exponential direction on the (hkl), crystal plane; (hkl), is a low exponential surface of the crystalline phase, (uvw), is a low exponential direction on the (hkl), crystal plane; (iuvw), is the atomic distance along (uvw), direction; (iuvw), is the atomic distance along the [uvw], direction; and $\theta$ is the angle between any two orientation indices [uvw], and {uvw}, in the cubic system. Bramfit [22] showed that the core with $\delta < 6\%$ is the most effective, $\delta = 6\%–12\%$ is moderately effective, and $\delta > 12\%$ is ineffective in heterogeneous nucleation. In order to calculate the mismatch, the lattice parameters of substrates and nucleated phases are required, as shown in table 5.

Table 6 and figure 1 show the mismatches between the (0001) surface of Ce2O3 and the (100), (110), and (111) surfaces of γ–Fe are more than 12% and 5.17%, respectively. Therefore, the (111) surface of γ–Fe is a habit plane, austenite grows along the surface, and the degree of the effectiveness of Ce2O3 as a heterogeneous nucleation core of primary austenite is high. Similarly, the crystallographic matching parameters between the (100) surface of CeS, the (0001) surface of Ce2O2S, and the (100), (110), and (111) surfaces of γ–Fe can be calculated (table 7).
Table 7 shows that the mismatch between the (100) surface of CeS and the three surfaces of γ–Fe is more than 12%. The two-dimensional mismatch between Ce₂O₂S (0001) and γ–Fe (111) is 8.3%, whereas the mismatch between the (0001) surface of Ce₂O₂S and the (100) and (110) surfaces of γ–Fe is more than 12%. This difference shows that Ce₂O₂S can become the heterogeneous nucleation core of primary austenite, and its effectiveness is moderate. In comparison with Ce₂O₃ and Ce₂O₂S, CeS cannot be the heterogeneous nucleation core of primary austenite. Therefore, the (111) plane of γ–Fe is a habit plane, and austenite grows in this direction.

According to the calculation of the nucleation effectiveness of Ce oxide on γ austenite, Ce₂O₂S and Ce₂O₃ can become the nucleation core of γ austenite, and the Ce₂O₃ nucleation core is the most effective. The addition of Ce can induce austenite nucleation and refine austenite grain.

3.3. Phase analysis of Fe–Mn damping alloy

The damping source of Fe–Mn alloy shows that the ε martensite plays the main damping role. The damping property of the alloy can be improved by increasing the number of ε martensite and changing the morphological characteristics of ε martensite [23]. Some studies [24] show that Ce compounds in solid solution tend to aggregate at the grain boundary. In figure 2(b) Ce oxides and Ce sulfide exist at the grain boundary, in figure 2(c) there is no Ce element in the crystal. The calculation based on two-dimensional mismatch degree theory reveals that Ce exists in the form of Ce oxide and Ce sulfide, the solid solution of a Ce compound tends to aggregate at grain boundaries, and they elicit a certain refinement effect on an austenite grain. The finer the austenite grain is, the higher the amount of martensite formation during shear will be and the thinner and finer the slab will be. The XRD phase analysis of Fe–Mn alloy was performed under the condition of ice-water rapid cooling held for 1 h at different solid solution temperatures. The results are shown in figure 3.

In figures 3(a) and (b), the three alloys are composed of α, γ, and ε phases. The diffraction peaks of the three alloys after solid solution treatment are stronger than those of the alloys without a solid solution treatment with
either $\gamma$ austenite or $\varepsilon$ martensite. Other conditions remain unchanged as the content of $\varepsilon$ martensite increased, and the strength of a microdamper source and elastic energy consume increased.

3.4. Microstructural and morphological analysis of Fe–Mn damping alloy

When the heat treatment temperature reaches 1050 °C, the alloy structure is completely transformed into an austenite structure [25]. Figure 4(a) shows that the amount of microstructure martensite in Fe–15Mn alloy after solution and rapid cooling is relatively large, the thickness of martensite lath is 3–4 $\mu$m, a few movable interfaces are found in martensite, and the vibration energy consumption is less, so the internal friction is relatively low.

The comparison of figures 4(b) and (c) reveals that the quenching structure of Fe–18Mn alloy is evidently refined by adding Ce. The number of lath martensite lamellae is increased, the spacing is less thin, the thickness is approximately 1–2 $\mu$m, and their shape is triangular.

The rare earth Ce element added to the alloy refines the austenite grains, which increases the nucleation core. As a result, the number of stacking faults increases during martensitic transformation from $\gamma$ to $\varepsilon$, and the amount of martensite increases [26].

4. Conclusion

(1) Thermodynamic calculations show that Ce can spontaneously form CeS, CeO$_2$S, Ce$_2$O$_3$, and other compounds. The order of generation is generally CeS, CeO$_2$S, and Ce$_2$O$_3$. However, MnS cannot be generated under the same conditions.

(2) The nucleation efficiency of Ce oxide and $\gamma$ austenite is calculated in accordance with two-dimensional mismatch theory. The results show that Ce$_2$O$_3$ and Ce$_2$O$_3$ can become the nucleation core of $\gamma$ austenite, and the nucleation efficiency of Ce$_2$O$_3$ is the highest. CeS cannot become the nucleation core of primary $\gamma$ austenite.
(3) The quenched structure of alloy is refined by the addition of Ce. The nucleation core of austenite increases, thereby increasing the driving force of martensitic transformation. Consequently, the number of lath martensite lamellae increases. They achieve a thickness of approximately 1–2 μm and mostly have a triangular shape.

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