Study on microstructure of NiAl matrix high temperature lubricating composites containing BaO/TiO2 metallic oxide

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Abstract

The microstructure of NiAl matrix high temperature lubricating composites containing BaO/TiO2 metallic oxides were investigated. The NiAl-BaO/TiO2 composites were fabricated by vacuum hot-pressing sintering. The diffraction peaks of NiAl slightly shifted to the left with the addition of BaO/TiO2 metallic oxide. The crystal plane distance of NiAl phase in the composite was bigger than that in NiAl material according to the Bragg equation. Meanwhile, the lattice distortion and dislocation occurred in the composite structure, which is probably due to the Ti element dissolve in the NiAl matrix during sintering. The cohesive energy and formation enthalpy of NiAl were improved with the incremental of Ti solution contents through density functional theory calculations, which was indicated that the Ti element could dissolve in the NiAl and was in good accordance with the results of XRD and TEM.

1. Introduction

High temperature lubricating composite has an important effect in the most industrial applications, such as aerospace and nuclear industries [1–3]. At present, the matrix material of high temperature lubricating composite is mainly Ni-based alloy, which is used below 1000 °C and very difficult to meet the needs of industrial development [6, 7]. NiAl intermetallic compound has high melting point (1638 °C), high thermal conductivity, low density (5.86 g cm−3), as well as excellent corrosion and oxidation at high temperature [8–13]. Nevertheless, the NiAl-based high temperature composites usually suffer the severe wear at high temperature [14–16]. Erdemir provided a standard that the binary oxides could present the better lubricating performance with the increasing of difference in ionic potential [17, 18]. This approach still has some restrictions and not appropriate to explain the lubricating performance of all oxides, however, it could provide the reference for oxide lubricant choice and give certain guidance to the lubrication mechanism of oxides at high temperature [19, 20]. In the BaO/TiO2 binary oxide system, the ionic potential difference is high and barium oxide gives lower interaction parameter according to polarizability, meaning the theoretically excellent lubricating performance [17, 21]. Nevertheless, most of the current research are mainly focused on the effect of binary oxide on the tribological properties of high temperature composite and have less report on the microstructure [22–25]. Therefore, the objective of this work fabricated the NiAl-BaO/TiO2 composite and investigated the microstructure of composites.

2. Materials and methods

The NiAl-BaO/TiO2 composites were fabricated by vacuum hot-pressing sintering. The images of the hot-press sintering furnace and samples were shown in figure 1. The dense and uniform of the samples were obtained by vacuum hot-pressing sintering technology. NiAl intermetallic compound, BaO and TiO2 were purchased from...
Shanghai cw-nano. The powders were blended at a mass fraction of 80% NiAl intermetallic compound and 20% BaO/TiO$_2$ (molar ratio BaO:TiO$_2$ = 1:1) through high energy ball-milled for 3 h, which could blend the powders uniformly. The ball was zirconium dioxide. The ratio of ball and powder was 10:1. The vial rotation speed was 200 rpm. Milling and pause was carried out alternately every one half hour. The 20 ml methanol was added before milling process. The mixed powder was enclosed in a graphite die and then sintered at 1300 °C for 1 h under the pressure of 20 MPa in hot-press sintering furnace. The dynamic vacuum of hot-press sintering furnace was about 10$^{-2}$ Pa. The x-ray diffractometer (Philips X’Pert-MRD) with a scan rate of 10° min$^{-1}$ using Cu-Ka radiation at 40 kV operating voltage was used to determine the phase composition of composite. The scanning electron microscope (Zeiss Gemini SEM 500) and high resolution transmission electron microscope (HRTEM, JEOL-2010 TEM) were utilized to observe the microstructure of composite. The cohesive energy and formation enthalpy of NiAl with the increasing Ti solution contents were estimated by Cambridge serial total energy package (CASTEP) within density functional theory. The kinetic energy cut-off value of 600 eV was used for plane wave expansion in reciprocal space. The sampling k-point mesh in the first irreducible Brillouin zone (BZ) was generated by Monkhorst-Pack method, using a 6 × 6 × 6 grid for each structure.

3. Results and discussion

Figure 2 shows the XRD patterns of NiAl and NiAl-BaO/TiO$_2$ composites. The NiAl material mainly contains the NiAl peaks (figure 2(a)). Interestingly, it can’t be obviously seen the diffraction peaks of BaO and TiO$_2$ in NiAl composite. On the contrary, the diffraction peaks of BaTiO$_3$ appear. It is probably due to the BaO and TiO$_2$ occur the reaction and produce the BaTiO$_3$ in the process of sintering. In order to further explain the reaction of BaO and TiO$_2$ in the NiAl composite, the Gibbs free energy ($\Delta G$) of this reaction at 1000 K is calculated according to the thermodynamic date. This reaction can be illustrated as follow:
The Gibbs free energy for this reaction at 1000 K is negative, indicating this reaction could possibly occur in the process of sintering. Meanwhile, the diffraction peaks of NiAl slightly shift to the left (figure 2(b)). It is probably due to the elements dissolve in the NiAl matrix [26–28]. The crystal plane distance of NiAl phase is 0.2462 nm and is bigger than that in NiAl material of 0.2451 nm according to the Bragg equation.

Figure 3 gives the SEM micrographs of NiAl material (a) NiAl-BaO/TiO2 composite (b) and corresponding element maps.

\[ \text{BaO} + \text{TiO}_2 \rightarrow \text{BaTiO}_3, \quad \Delta G_T = -140.857 \text{ KJ mol}^{-1}(1000 \text{ K}) \]  \hspace{1cm} (1)

In order to further investigate the microstructure of composite, the TEM analysis is conducted. Figure 4(a) displays the TEM micrograph of NiAl-BaO/TiO2 composite. It has no precipitated phase in the matrix. Furthermore, as shown in figure 4(b), the SAED pattern in the zone axis [001] confirms that the region A in figure 4(a) is the NiAl matrix. To our surprise, the NiAl matrix contains Ti element according the EDS of region...
A in figures 4(a) (c). It is probably due to the Ti element dissolve in the NiAl matrix during sintering. This result could explain the phenomenon of diffraction peaks of NiAl slightly shift to the left with the addition of BaO/TiO₂ (figure 2). Figure 4(d) presents the HRTEM of micrograph of region A in figure 4(a). Further, the inverse FFT micrograph of region B and C in figure 4(d) are shown in figures 4(e) and (f), respectively. According to the inverse FFT micrograph of region B (figure 4(e)), the measured crystal plane distance of NiAl matrix is 0.2465 nm, which is well consistent with the calculated value based on the XRD analysis in figure 2(b). Besides, it is worth mentioning that the lattice distortion obviously occurs in the composite structure according to the inverse FFT micrograph of region C (figure 4(f)). It’s probably due to the Ti element dissolve in the NiAl matrix during sintering, which is in good accordance with the results of XRD (figure 2) and EDS (figure 4(c)). Meanwhile, the dislocation can be observed and the T indicates the position of dislocation (figure 4(f)). The dislocation could play a significant role in the improvement of mechanical properties of composite [27].

To explore Ti dissolve ability and structural stability of NiAl phase, the cohesive energy and formation enthalpy of NiAl with the increasing Ti dissolve contents are estimated by calculating total energy of bulk NiAlTiₓ phases, as listed in table 1. As defined in equations (2) and (3), the much smaller negative values of these two parameters indicate the high stability of the phases. Especially, negative values of ΔrH suggest that the formation of NiAlTiₓ from reactants is energetically favorable. Besides, the NiAlTi1 and NiAlTi2 phases are more stable than NiAl phase, which show negative enthalpy value of −0.65 and −0.63 eV atom⁻¹, respectively. Therefore, a much smaller formation enthalpy always results in a significantly dissolve ability. The cohesive energy and formation enthalpy of NiAl were improved with the incremental of Ti solution contents through density functional theory calculations, which was indicated that the Ti element could dissolve in the NiAl and was in good accordance with the results of XRD (figure 2) and TEM (figure 4).

\[
E_{\text{coh}}(\text{NiAlTi}_x) = E_{\text{coh}}(\text{NiAl}) - E_{\text{coh}}(\text{Ni}) - x E_{\text{coh}}(\text{Ti}) \tag{2}
\]

\[
\Delta_rH (\text{NiAlTi}_x) = E_{\text{coh}}(\text{NiAlTi}_x) - E_{\text{coh}}(\text{Ni}) - E_{\text{coh}}(\text{Al}) - x E_{\text{coh}}(\text{Ti}) \tag{3}
\]

4. Conclusions

In summary, the microstructure of NiAl matrix high temperature lubricating composites containing BaO/TiO₂ metallic oxides are investigated. The diffraction peaks of NiAl slightly shift to the left with the addition of BaO/TiO₂. Meanwhile, the crystal plane distance of NiAl phase is 0.2462 nm and is bigger than that in NiAl material of 0.2451 nm according to the Bragg equation. It’s probably due to the Ti element dissolve in the NiAl matrix during sintering. The lattice distortion and dislocation occur in the composite structure. It’s probably due to the Ti element dissolve in the NiAl matrix during sintering, which is in good accordance with the results of XRD. The cohesive energy and formation enthalpy of NiAl are improved with the increasing of Ti solution contents through density functional theory calculations, which is indicated that the Ti element could dissolve in the NiAl matrix and is in good accordance with the results of XRD and TEM.

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| Table 1. Cohesive energy and formation enthalpy of NiAlTi phases. |
|----------------------|----------------------|
| Phase               | Cohesive energy(eV) | Formation enthalpy(eV) |
| NiAl                | −6.16               | −0.66                 |
| NiAlTi1             | −6.15               | −0.65                 |
| NiAlTi2             | −6.13               | −0.63                 |
| NiAlTi3             | −6.11               | −0.62                 |
| TiAl                | −5.7                | −0.40                 |
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