Effects of Cr and Al Contents on the Preparation of SiC Fiber-Reinforced NiCrAl Alloy Matrix Composite

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Abstract

In this work, the effects of Cr and Al contents on the preparation of SiC fiber-reinforced NiCrAl alloy matrix composites (SiC_f/Ni–20Cr–5Al, SiC_f/Ni–15Cr–5Al, SiC_f/Ni–10Cr–5Al and SiC_f/Ni–10Cr–3Al) were thoroughly discussed. The composites were prepared by vacuum hot pressing process using matrix-coated fibers. It was found that Cr solute atoms played a significant role in retarding the recrystallization of NiCrAl alloy matrix, and the Al elements in the form of γ' -Ni₃Al phase had a suppression effect on the plastic flow of the matrix. Therefore, the reduction in Cr and Al contents was conducive to the recrystallization and plastic flow of NiCrAl alloy matrix, thereby reduced the size and number of micro-voids in the composite. In addition, this work provides some guidance for designing and manufacturing reasonable SiC fiber-reinforced Ni alloy matrix composites.

Keywords SiC fiber · NiCrAl alloy · Composite · Recrystallization · Plastic flow

1 Introduction

Tremendous demands are required on the development of materials with lightweight and high thrust-to-weight ratio in the aircraft and aerospace industries [1–6]. Generally speaking, Ni alloys are the most widely used aeronautical materials due to the excellent high-temperature mechanical property and corrosion resistance [7–12]. In recent years, continuous fiber-reinforced Ni alloy matrix composite becomes a potential substitute material in order to realize the mass-reduction goal for advanced aircraft engines. The similar composites have been prepared and investigated in the prior works [13–15]. For example, Zhang et al. prepared the SiC fiber-reinforced Ni matrix composite and researched

the plastic deformation mechanism of the matrix during the vacuum hot pressing (VHP) process [13]. Li et al. fabricated the SiC fiber-reinforced GH4738 matrix composite by means of hot isostatic pressing, measured the tensile strength of the material and analyzed the interfacial behavior [14]. Niu et al. prepared the SiC fiber-reinforced NiCrAl matrix composite and measured the interfacial residual stress on the basis of Raman spectroscopy [15]. The bulk of these studies is concerned with the preparation techniques and mechanical properties of the composites. However, the perfect composites with sufficient diffusion bonding of Ni alloy matrix have not been achieved to date, none of the above works pay attention to the effect of different matrices on the diffusion bonding process in preparation.

As is known to all, Cr and Al are the most common constituent elements in Ni alloys. They can form a native, adherent oxidation protective film on the surface of the alloys and keep them from oxidizing in the service environment [16]. To be precise, Cr element plays a positive role in solid solution strengthening and significantly enhances the thermal corrosion resistance of Ni alloys [16, 17]. Besides, Al is one of the elements to form γ' -Ni₃Al precipitates which act as precipitation-strengthened phases in the material, and the introduction of Al element can improve the resistance capability of high-temperature oxidation [18, 19]. Therefore, different Cr and Al contents will lead to the microstructure

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difference of Ni alloy matrices in the composites, which affects the diffusion bonding process and eventually gives rise to the different mechanical properties. Undoubtedly, it may have a significant meaning to investigate the effect of Ni alloys with different Cr and Al contents on the composite fabrication process.

In this work, NiCrAl alloys with different Cr and Al contents, i.e., Ni–20Cr–5Al, Ni–15Cr–5Al, Ni–10Cr–5Al and Ni–10Cr–3Al, were first designed as the matrices of SiC fiber-reinforced composites. Then, the parameters of the VHP process were optimized, and the effects of Cr and Al content on the preparation of the composites were investigated. The present research provides an important opportunity to advance the understanding of the diffusion bonding process of NiCrAl alloy matrix in continuous fiber-reinforced Ni alloy matrix composites.

2 Experimental

The continuous SiC fibers (W core) used in present work were manufactured by chemical vapor deposition (CVD) in Institute of Metal Research, Chinese Academy of Sciences (IMR, CAS). The total diameter of the fiber is $\sim 100\ \mu\text{m}$, including the $12\ \mu\text{m}$ diameter of a W core and the $2\ \mu\text{m}$ thickness of a carbon protective layer on the surface. The

average tensile strength of the fibers is up to 3.6 GPa with high Weibull modulus [20].

The detailed process of preparing the composites is illustrated in Fig. 1. In Stage 1, the matrix-coated fiber was fabricated by depositing a $\sim 2\ \mu\text{m}$ thickness $(\text{Al} + \text{Al}_2\text{O}_3)$ diffusion barrier coating and a $\sim 30\ \mu\text{m}$ thickness NiCrAl coating on the surface in succession by means of dual-target magnetron sputtering technique. The $(\text{Al} + \text{Al}_2\text{O}_3)$ diffusion barrier has been demonstrated to be effective to prevent the intense interfacial reactions between Ni alloy and SiC fibers in our previous work [13]. The purity of Al sputtering targets was 99.99 wt.%, and the NiCrAl sputtering targets had a nominal composition of Ni–20Cr–5Al, Ni–15Cr–5Al, Ni–10Cr–5Al and Ni–10Cr–3Al. All of the targets were rectangular with a size of $270\ \text{mm} \times 70\ \text{mm}$. Subsequently, as shown in Stage 2, the matrix-coated fibers were bonded tightly in a plane to form precast slabs using an organic binder, and then, the slabs were stacked up by hexagonal arrangement and encapsulated utilizing Ni foils. Finally, the capsule was put into the die of the graphite jig and consolidated into a composite by VHP process. The main parameters of the VHP process were temperature, pressure and holding time. All of them were optimized in the preparation of the composites.

The interface and transverse-section morphologies of the composites were observed by field-emission scanning electron microscopy (FE-SEM, PEG XL30). Elemental

Fig. 1 Schematic diagram of the process of preparing the composite

distribution and chemical composition were inspected by energy dispersive spectrometer (EDS) mounted on the FE-SEM. The phase compositions of the composites were identified by X-ray diffraction (XRD, D/MAX-RA).

3 Results and Discussion

3.1 Morphologies and Phase Compositions of the Composites

The chemical compositions of the NiCrAl coatings on the surface of the matrix-coated fibers are detected by EDS and listed in Table 1, in which the mass percentages of Ni, Cr

Table 1 Chemical compositions of the NiCrAl coatings on the surface of the matrix-coated fibers (wt.%)

Element	Ni–20Cr–5Al	Ni–15Cr–5Al	Ni–10Cr–5Al	Ni–10Cr–3Al
Ni	74.40	79.84	84.42	86.53
Cr	20.87	14.78	10.47	10.79
Al	4.73	5.38	5.11	2.68

and Al are in good agreement with that of the sputtering targets. Figure 2 shows the morphologies of the composites with different Cr and Al contents prepared on the condition of 940 °C/60 MPa/2 h, respectively. It can be seen that all of the four composites bond unsatisfactorily, there still exist some micro-voids in the composites. However, no interfacial reactions take place between the SiC fibers and the matrix except for a few locations, where the (Al + Al₂O₃) diffusion barriers break up caused by the matrix deformation. And as the contents of Cr and Al decrease, the micro-voids become fewer and smaller, associated with the occurrence of partial recrystallization in the columnar grains which formed during the magnetron sputtering process. In addition, some distinct inter-diffusion zones appear in the contact areas of the matrix, as shown in Fig. 2c, d.

Figure 3 presents the XRD patterns of the above four composites. The phase compositions of the different NiCrAl alloy matrices in four composites are all coherent and ordered γ/γ' solid solutions, among which γ' -Ni₃Al acts as a precipitation-strengthened phase and Cr as a second-phase particle solubilizes in γ/γ' phases, and the difference is the numbers of γ' -Ni₃Al phases and Cr solute atoms. This kind of microstructure features high flow stress in the plastic

Fig. 2 Morphologies of **a** SiC_f/Ni–20Cr–5Al, **b** SiC_f/Ni–15Cr–5Al, **c** SiC_f/Ni–10Cr–5Al, **d** SiC_f/Ni–10Cr–3Al composites prepared on the condition of 940 °C/60 MPa/2 h

Fig. 3 XRD patterns of the four kinds of SiC_f/NiCrAl composites

Table 2 Phase compositions and proportions of NiCrAl alloys with different Cr and Al contents (at.%)

Phase	Ni-20Cr-5Al	Ni-15Cr-5Al	Ni-10Cr-5Al	Ni-10Cr-3Al
γ'-Ni ₃ Al	10.02	10.08	10.14	6.22
γ	89.98	89.92	89.86	93.78

deformation process, resulting in a poor plastic-flow performance of the matrix [21]. Table 2 lists the phase compositions and proportions of NiCrAl alloys matrices with different Cr and Al contents. Comparing the composites of SiC_f/Ni-20Cr-5Al, SiC_f/Ni-15Cr-5Al and SiC_f/Ni-10Cr-5Al, the proportions of γ'-Ni₃Al are about the same (~10 at.%), while the number of Cr solute atoms reduce gradually. As seen in Fig. 2a–c, partial recrystallization of the matrices occurs in SiC_f/Ni-15Cr-5Al and SiC_f/Ni-10Cr-5Al composites under the same VHP parameters, but the micro-voids still exist in three composites, which implies that the recrystallization temperature of Ni-20Cr-5Al alloy is higher than that of other two NiCrAl alloys, and Cr solute atoms retard the recrystallization of the matrices.

It is well known that the solute atoms commonly segregate to the grain boundaries at hot deformation temperature and decrease their mobility [22]. Hence, the above phenomenon is probably caused by the high solute pinning effect, which applies solute drag pressure on migrating grain boundaries, and thereby degrades the potential of

recrystallization. In addition, the interaction of solute atoms with dislocations may also play a role. The similar results have happened in other alloys during high-temperature deformation [22–24]. Accordingly, it can be deduced that the lower the Cr solute atoms in the matrix, the higher the tendency for grain growth and recrystallization during the VHP process.

Besides, taking SiC_f/Ni-10Cr-5Al and SiC_f/Ni-10Cr-3Al composites into consideration (Fig. 2c, d), the numbers of Cr solute atoms are almost same, but the proportions of γ'-Ni₃Al decrease. It can be observed that the inter-diffusion zones in the contact areas of the matrix increase while the size and number of micro-voids decrease, which indicates that the reduction in γ'-Ni₃Al precipitates promotes the plastic flow of the matrix. Generally, dislocation can be impeded by the γ/γ' interfaces, leading to the improvement of tensile strength of superalloy, i.e., γ'-Ni₃Al precipitation strengthening [25, 26]. As a consequence, with the decrease of Al content, the precipitation strengthening of γ'-Ni₃Al would become weak, and the plastic flow of the matrix would be strengthened, resulting in the increase in the composites density.

Comparatively speaking, the effect of γ'-Ni₃Al precipitation strengthening is more significant than solid solution strengthening of Cr atoms in the four composites, so the plastic-flow phenomenon of the NiCrAl alloy matrix is more obvious when reducing the content of Al at constant Cr.

Figure 4 exhibits the morphologies of the SiC_f/Ni-20Cr-5Al and SiC_f/Ni-10Cr-3Al composites prepared on the condition of 990 °C/60 MPa/2 h. It can be observed that severe interfacial reactions have taken place between the SiC fibers and the Ni-20Cr-5Al alloys (Fig. 4a). In the SiC_f/Ni-10Cr-3Al composite (Fig. 4b), by contrast, the fibers keep intact with the (Al + Al₂O₃) diffusion barriers, the matrix is subjected to plastic deformation, no obvious interfacial reactions occur and only a few micro-voids appear. All the above results clearly indicate the (Al + Al₂O₃) diffusion barrier still works at 990 °C, and the Ni-20Cr-5Al alloy matrix is hard to produce sufficient plastic deformation at 990 °C, leading to the crack of the (Al + Al₂O₃) diffusion barrier under increasing pressure and the occurrence of the interfacial reactions between the fibers and matrix.

For the Ni-10Cr-3Al alloy matrix, however, the numbers of γ'-Ni₃Al phases and Cr solute atoms are relatively small, so the plastic-flow performance of the alloy is better and the recrystallization is more likely to take place, thereby filling up the micro-voids in the composites and achieving close combination. Hence, it can be deduced that the presence of precipitation-strengthened element Al and solid

Fig. 4 Morphologies of **a** SiC_f/Ni-20Cr-5Al, **b** SiC_f/Ni-10Cr-3Al composites prepared on the condition of 990 °C/60 MPa/2 h

Fig. 5 Transverse-section morphologies of **a** SiC_f/Ni-20Cr-5Al, **b** SiC_f/Ni-15Cr-5Al, **c** SiC_f/Ni-10Cr-5Al, **d** SiC_f/Ni-10Cr-3Al composites prepared on the condition of 960 °C/60 MPa/2 h

solution strengthening element Cr improves the deformation resistance of NiCrAl alloy, degrades its performance of plastic flow and increases the recrystallization temperature. A higher VHP temperature is needed to acquire a perfectly

bonded composite, whereas too high temperature (above 1000 °C) will damage the properties of the fibers and the performance of the composite [20], consequently, the addition of Cr and Al should not be excessive.

Fig. 6 Transverse-section morphologies of **a** Ni-20Cr-5Al, **b** Ni-15Cr-5Al, **c** Ni-10Cr-5Al, **d** Ni-10Cr-3Al matrices in different composites prepared on the condition of 960 °C/60 MPa/2 h

3.2 NiCrAl Alloy Matrix Evolution process of the Composites

Figure 5 presents the transverse-section morphologies of the composites with different Cr and Al contents prepared on the condition of 960 °C/60 MPa/2 h, respectively. As shown in Fig. 5a, the NiCrAl alloy matrix is in close contact with each other and maintains the columnar grain structure in SiC_f/Ni-20Cr-5Al composite. While reducing the content of Cr to 15 wt.% (Fig. 5b), the recrystallization happens in the contact areas of NiCrAl alloy matrix. Further reducing the Cr content to 10 wt.% (Fig. 5c), the recrystallization of the matrix is almost completed. Moreover, when reducing the content of Al to 3 wt.% at constant 10 wt.% Cr (Fig. 5d), the inter-diffusion of NiCrAl alloy matrix is sufficient, and the whole composite is more compact.

Diffusion bonding is a process by which two nominally flat surfaces are joined at elevated temperatures under an external pressure [27]. Several theoretical models were developed to quantify the contribution of different mechanisms to densification during the consolidation process for matrix-coated fiber-reinforced composites [28–30]. These

models, in particular that of Chen et al. [28], give good predictions. Based on the model of Chen et al. [28], the NiCrAl alloy matrix evolution process of the composites in the present work can be clarified into three stages.

The transverse-section morphologies of NiCrAl alloy matrices in different composites on the condition of 960 °C/60 MPa/2 h are displayed in Fig. 6. At the first stage (Fig. 6a), the contents of Cr and Al are relatively high. The high strength, derived from the fine grain structure and a combination of solid solution strengthening of Cr atoms and precipitation hardening of γ' -Ni₃Al precipitates, makes it difficult for Ni-20Cr-5Al matrix to produce evident plastic flow after contact under pressure, and the recrystallization does not happen because the temperature is lower than the recrystallization temperature. At the second stage, the reduction in the Cr solute atoms weakens the solid solution strengthening effect and causes the coarsening of γ' -Ni₃Al precipitates (Fig. 6b, c), making the yield strength of the NiCrAl alloy matrix lower than the external pressure and producing plastic flow. Additionally, the recrystallization happens because the reduction in Cr solute atoms lowers the recrystallization temperature

of the matrix. At the last stage, with the reduction of Al content (Fig. 6d), the number of γ' -Ni₃Al precipitates decreases, and their effect on impeding the motion of dislocation weakens, resulting into sufficient plastic flow of the matrix under external pressure.

4 Conclusions

In the present work, four kinds of composites with different Cr and Al contents, i.e., SiC_f/Ni–20Cr–5Al, SiC_f/Ni–15Cr–5Al, SiC_f/Ni–10Cr–5Al and SiC_f/Ni–10Cr–3Al, were prepared by means of VHP process using matrix-coated fibers. And the effects of Cr and Al contents on the preparation of the composites were investigated. The major conclusions can be listed as follows:

1. The (Al + Al₂O₃) diffusion barrier can still prevent the excessive interfacial reactions between the SiC fibers and NiCrAl alloy at 990 °C.
2. During the preparation of SiC_f/NiCrAl composites, Cr solute atoms play a significant role in retarding the recrystallization of the NiCrAl alloy matrix, and the Al elements in the form of γ' -Ni₃Al phase have a suppression effect on the plastic flow of the matrix.
3. The effect of γ' -Ni₃Al precipitation strengthening is more significant than solid solution strengthening of Cr atoms in the four composites. As a consequence, more sufficient diffusion within the matrix and denser composite with reducing the content of Al rather than reducing the content of Cr can be obtained.

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