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Wettability and interfacial reactions of PdNi-based brazing fillers on C-C composite

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Abstract: The wettability and interfacial reactions of four kinds of PdNi-based brazing fillers on C-C composite were studied with the sessile drop method. The results showed that the wettability of these brazing fillers was improved with the increase of Cr content. Cr distributed at the interface of brazing filler/C-C composite and the formation of $Cr_{23}C_6$ phase was speculated. In the interface between Ni-33Cr-24Pd-4Si brazing filler and C-C composite, element Cr reacted with C-C to form Cr-C reaction layer. Pd together with Si participated in the interfacial reactions and formed Pd_2Si and Pd_3Si phases. Furthermore, in this reaction zone, the residual brazing alloy became Ni-rich and Pd-depleted.

Key words: PdNi-based brazing filler; diffusion layer; wettability; interfacial reaction

1 Introduction

Carbon-carbon(C-C) composites have high strength at elevated temperatures, good thermal-shock resistance, low density and thermal expansion coefficient, excellent corrosion resistance and frictional behavior. They are attractive as structural materials for high-temperature aerospace application[1−2].

The application of C-C composites, to some extent, will be dependent on their joining technology[3−5]. Brazing and diffusion bonding methods have received much attention in joining of C-C composite and superalloy. So far, the research progress has been rather slow. Brazing, because of its simplicity and small capital investment, is received extensive attention as lower heating-up temperature joining method than diffusion bonding especially for C-C composite/superalloy joints.

Cu-based[6], AgCu-based[7] and Ti-based[8−9] brazing fillers were chosen to braze C-C composites, but the service temperature of these joints was less than 500 ℃. The C-C composite joints were also obtained with Si, Mg_2Si[10] and $TiSi_2$[11] brazing fillers, but the heating-up temperature even reached 1 420−1 490 ℃, which would deteriorate the microstructure of superalloys. Therefore, it is necessary to develop new high-temperature brazing fillers for C-C composite joining.

Considering that Pd-Ni alloys have high mechanical properties and can give high service temperatures, three kinds of Cr-active PdNi-based brazing fillers are designed, with different Cr contents. The wettability of these alloys as well as one Ni-Cr-Pd system brazing filler (Ni-33Cr-24Pd-4Si, mass fraction, %) on C-C composite is studied in this work.

2 Experimental

The samples are made of three-dimensional orthogonal reinforced C-C composite with a density of 2.0 g/cm^3 and a size of 17 mm×13 mm×2 mm. Four kinds of brazing fillers (Pd-40Ni, PdNi-(4−11)Cr, PdNi-(12−25)Cr, and Ni-33Cr-24Pd-4Si, mass fraction, %) were designed and prepared with mixed metal powders by the following process. The high-purity (>99.5%) powders (75 μm) of Pd, Ni, Cr and Si were weighed in the designed ratio and blended mechanically, then, the mixed powder was pressed into a cylindrical pellet with a diameter of 4 mm. The samples were heated to a certain temperature at a heating rate of 10 K/min and held for 30 min and cooled down to room-temperature at a rate of 5 K/min. Their contact angles on C-C composite were measured with the sessile drop method.

After the heating cycle, each sample was cross-

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sectioned, polished, and examined by a scanning electron microscope(SEM) equipped with an X-ray energy-dispersive spectrometer(XEDS).

3 Results and discussion

Pd-40Ni and PdNi-(4−11)Cr gave higher contact angles of 69° and 75°, respectively (Table 1) and condensed hemispheric grains (Figs.1(a) and (b)) after being held at 1 250 ℃ for 30 min in vacuum. Noticeably, PdNi-(12−25)Cr and Ni-33Cr-24Pd-4Si showed excellent wettability (Figs.1(c) and (d)) with low contact angles of 2°−3° (Table 1). Therefore, evidently, the content of active element Cr has a great influence on wettability of the four kinds of brazing fillers.

Table 1 Contact angles of four kinds of brazing fillers on C-C composites

Brazing filler	Contact angle/(°)	Remark
Pd-40Ni	69	−
PdNi-(4−11)Cr	75	−
PdNi-(12−25)Cr	3	Excellent
Ni-33Cr-24Pd-4Si	2	Excellent

The microstructures of the polished cross-sections of Pd-40Ni, PdNi-(4−11)Cr, PdNi-(12−25)Cr and Ni-33Cr-24Pd-4Si on C-C composite are shown in Fig.2 and the compositions of micro-zones in Fig.2 are listed in Table 2. The diffusion layer was not formed at the Pd-40Ni/C-C composite interface and some Pd-40Ni alloy infiltrated into the surface layer of the C-C matrix (Fig.2(a)). The PdNi-(4−11)Cr/C-C composite interface consisted of the mash microstructure (labeled 1 in Fig.2(b)) and a few fibers of C-C matrix distributed in the base brazing filler (labeled 3 in Fig.2(b)). With the addition of Cr into the PdNi-based alloy, the interface gave some evidence of reaction. However, the EDS analysis results showed that the "reaction" layer was still composed of Pd-Ni phase but dissolved with Cr and C.

A typical banded reaction structure was observed at the PdNi-(12−25)Cr/C-C composite interface, consisting of Cr and C. The two elements formed Cr-C phases (No.4 in Table 2). Some island-shaped phases extricated into the brazing filler matrix (labeled 5 in Fig.2(c)) where Pd and Ni, Cr and C formed Pd-Ni solid solution and Cr-C phases, respectively (No.6 in Table 2).

As far as Ni-33Cr-24Pd-4Si was concerned, a homogeneous diffusion layer with 15−20 μm in width was formed at the Ni-33Cr-24Pd-4Si/C-C composite interface (labeled 7 in Fig.2(d)). Cr-C phases existed there too (No.7 in Table 2). The blocky zone 8 (Fig.2(d)) contained Pd-Si and Ni-Si phases. The grayish white zone (labeled 10 in Fig.2(d)) should be mainly composed of Pd-Si phases. Furthermore, due to the above interfacial reactions, the brazing filler matrix (labeled 9 in Fig.2(d)) became Ni-rich and Pd-depleted, where elements Cr and C with rather high concentrations were

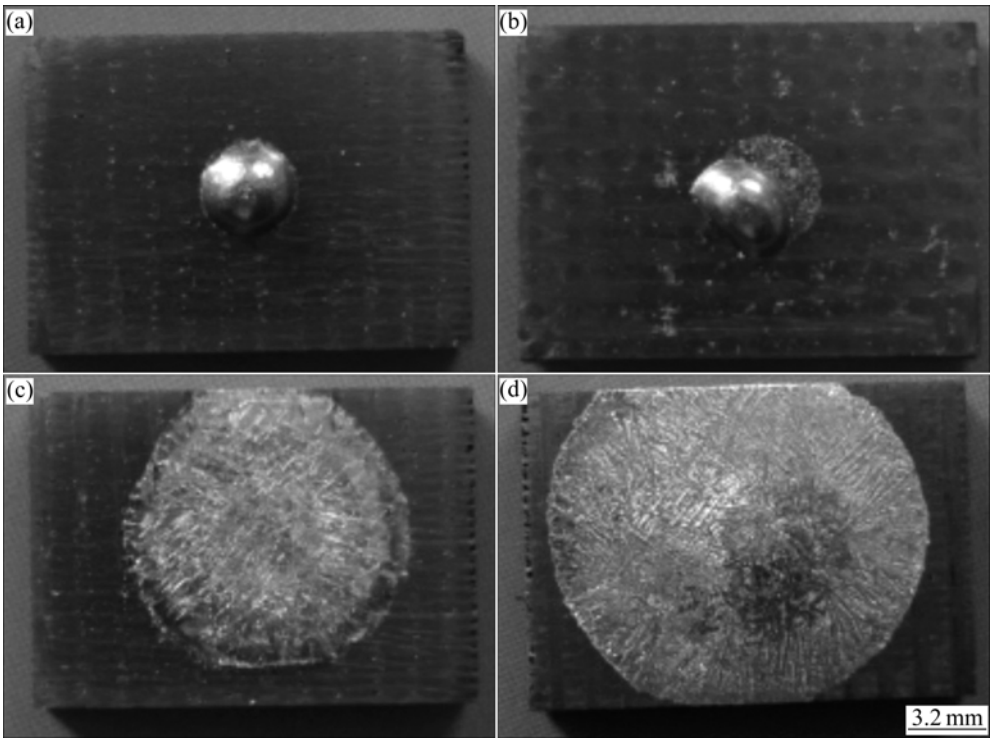

Fig.1 Photographs showing wettability of Pd-40Ni (a), PdNi-(4−11)Cr (b), PdNi-(12−25)Cr (c) and Ni-33Cr-24Pd-4Si (d) brazing fillers on C-C composites

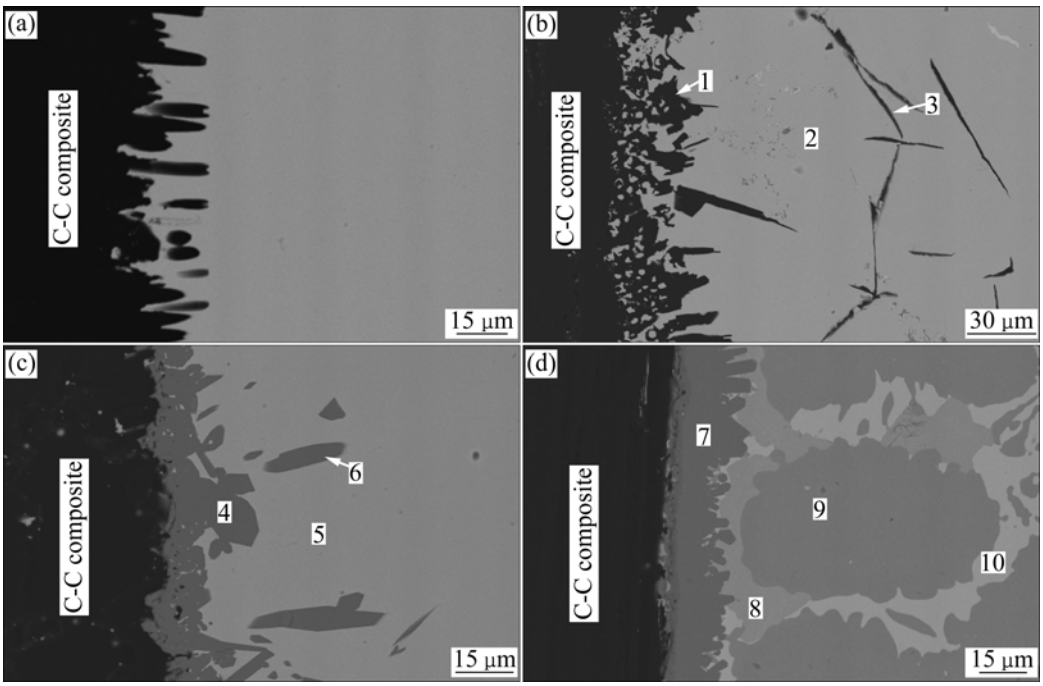

Fig.2 Back-scattered electron images of interfaces using four kinds of brazing fillers on C-C composites: (a) Pd-40Ni; (b) PdNi-(4−11)Cr; (c) PdNi-(12−25)Cr (d) Ni-33Cr-24Pd-4Si

Table 2 Compositions of characteristic zones at interface of four kinds of brazing fillers on C-C composites

Microzone No.	*x*/%						Possible phase
	C	Cr	Ni	Pd	Si	Total	
1	99.67	−	−	0.10	−	99.77	C-C matrix
2	31.15	10.22	28.06	28.08	−	97.51	Pd-Ni phase dissolved with Cr and C
3	96.89	0.31	0.76	1.53	−	99.49	C-C matrix
4	78.74	20.92	−	−	−	99.66	Cr-C phase
5	77.66	21.93	0.15	−	−	99.74	Cr-C phase
6	37.05	11.70	24.18	25.80	−	98.73	Pd-Ni phase dissolved with Cr and C
7	68.72	30.28	1.00	−	−	100.00	Cr-C phase
8	38.33	0.93	27.32	16.51	16.11	99.20	Pd-Si and Ni-Si phases dissolved with C
9	29.06	15.54	43.06	6.26	5.30	99.22	Ni-rich phase
10	19.91	−	9.00	46.18	24.91	100.00	Pd-Si phase

also detectable.

For the wetting interfaces containing some Cr element, according to EDS analysis (Table 2), the reaction bands (labeled 4 and 7 in Figs.2(c) and (d), respectively) are believed to be Cr-C compounds. It is known that there exist four different types of Cr carbides, namely, $Cr_{23}C_6$, Cr_4C, Cr_7C_3 and Cr_3C_2. Using thermo-chemistry data, the Gibbs free energies of formation of various selected metal carbides can be calculated, for example, at 1 127 ℃, those of $Cr_{23}C_6$, Cr_4C, Cr_7C_3 and Cr_3C_2 are −460, −96, −70 and −12 kJ/mol, respectively[12]. Therefore, from the thermo-dynamical view point, the most likely carbide to form in the present system is $Cr_{23}C_6$. In general, active element Cr promotes the reaction of brazing fillers with C-C composite, resulting in the improvement of wettability on C-C matrix.

Firstly, at Ni-33Cr-24Pd-4Si/C-C composite interface close to the C-C surface, element Cr reacted with C-C and formed Cr-C reaction layer (band 7 in Fig.2(d)). Subsequently, Pd and Si participated in the reactions and formed Pd_2Si and Pd_3Si phases[13−15], and in this reaction zone, the residual brazing alloy became Ni-rich and Pd-depleted. Obviously, under the same heating condition of 1 250 ℃, 30 min, among the four brazing fillers, the reactions between the C-C

composite and Ni-33Cr-24Pd-4Si brazing filler should be the strongest.

4 Conclusions

1) The element Cr distributed at the interface between C-C composite and the brazing filler, and formed Cr-C phase. The wettability of the Pd-Ni based brazing fillers on C-C composites was improved with the increase of the content of active element Cr.

2) At the Ni-33Cr-24Pd-4Si/C-C composite interface, element Cr reacted with C-C and formed Cr-C reaction layer. Pd and Si participated in the reactions and formed Pd_2Si and Pd_3Si phases, and in this reaction zone, the residual brazing alloy became Ni-rich and Pd-depleted.

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