Effect of ZrB$_2$ Addition on Sintering Temperature and Densification of Vacuum-Fused NiCr/WC Cermet Coating

Z X Yu$^{1,2}$, J Meng$^1$$^*$, X C Sheng$^1$ and J Le$^1$

$^1$ Key Laboratory of Inorganic Coating Materials CAS, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 588 Heshuo Rord, Jiading District, Shanghai 201899, China
$^2$ University of Chinese Academy of Sciences, Beijing 100049, PR China
Email: jiameng@mail.sic.ac.cn

Abstract. NiCr/WC cermet coatings were fabricated by vacuum fusion sintering on the surface of nickel-base alloy at 1220 ℃. The sintering temperature, densification mechanism and oxidation resistances of the cermet coating with ZrB$_2$ additive were investigated using thermogravimetric and differential thermal analysis method, theoretical calculation of phase diagram with the FactSage software, X-ray diffraction, and scanning electron microscopy. The sintering temperature of NiCr/WC cermet coating with ZrB$_2$ additive decreased 123 ℃ and obtained the dense cermet coatings. The densification mechanism of NiCr/WC cermet coating added with ZrB$_2$ is mainly attributed to the reaction occurred between Ni and ZrB$_2$ and the ample liquid phases formed at 1220 ℃. The surface of the WC particles is coated by Cr$_x$C$_y$ and surrounded by NiCr alloy result in the better oxidation resistance of the cermet coating added with ZrB$_2$.

1. Introduction
Nickel-base alloys have been applied to various high-temperature structural material owing to its outstanding mechanical property and oxidation resistance [1-3]. However, the unmodified alloys do not have the functions of high temperature strength, fracture toughness, oxidation resistance and erosion resistance at the same time, leading that these kinds of alloys cannot meet the extremely stringent operating conditions [4]. One of the effective solutions is that the nickel-base alloy substrates are coated with protective coating. Such as the cermet coating which possesses the characteristics of both metal and ceramics, high strength, toughness, electrical conductivity and thermal conductivity of metal materials as binding phase, while high hardness, strength, wear resistance, corrosion resistance and chemical stability of ceramic materials as ceramic reinforced phase as well [5-10].

The main preparation methods of the cermet coatings contain high velocity oxy-fuel spraying (HVOF), high-velocity air fuel (HVAF), thermal spraying, laser cladding, electrochemical, and vacuum fusion sintering (VFS), etc. [11-15]. Compared with other methods, VFS possesses advantages such as low cost, easy operation, and no special requirement to the shape of the substrates [7].

In previous studies, most of the higher softening temperature alloys are used in the preparation of the substrate for the coatings, such as steel. The different kinds of cermet coatings can more easily sintered on the substrates below its softening temperature [16]. For VFS, It is the primary concern that the sintering temperature of the cermet coating must be lower than the softening temperature of
the substrate for protecting it. For the lower softening temperature alloys superalloys, it is essential to reduce the sintering temperature of the coatings below the softening temperature of substrates. In order to reduce the sintering temperature, the additive phases were selected to add into the cermet coatings, such as B, CeO₂, MgO, Rare Earth Metal Yttrium. However, there are few reports about the additives mechanism of effective in the cermet coatings [17-21].

In present study, to obtain the cermet coatings with excellent properties on nickel-base alloy by VFS, Ni and Cr were selected as the metal bonding phases in order to achieve a good metallurgical bonding between the coating and the substrate; WC was used as ceramic reinforced phase; and ZrB₂ was regarded as the additive to decrease the sintering temperature of the NiCr/WC cermet coatings [22]. The appropriate sintering temperature of the NiCr/WC cermet coating was investigated. Besides, densification mechanism was discussed in detail from both the theoretical arithmetic and experimental verification aspects, respectively. Moreover, oxidation resistance of the cermet coating with ZrB₂ additive were studied at the temperature range of 800°C-1000°C. It might provide some useful information for potential application of this material on more reactive metallic substrates besides superalloys.

2. Experiment

2.1. Preparation
The nickel-base alloy substrates were acid pickling by self-configuring mixed acid to remove impurities and oxide scales on the surface before coating. The proportion (0.49/0.51) of the Ni to Cr corresponding to the low melting point (1345 °C) in the NiCr phase diagram was selected as the ratio of the NiCr powders in the coating system [11]. 28.00 wt% Ni powders, 29.14wt% Cr powders, 38.10 wt% WC powders, 4.76 wt% ZrB₂ powders and a small amount of alcohol were directly mixed for 72 h by using a rolling ball mill to obtain uniform wet composite powders. Then the wet composite powders were natural withering for drying ones and a few varnish as caking agent was added into the above dry composite powders to prepare the coating slurry. After, the cleaned substrate was dipped in obtained slurry and sintered at 1220 ℃ for 10min in a vaccum high-temperature furnace. Eventually, the cermet coating was formed on the surface of nickel-base alloy.

2.2. Characterization
Thermo-gravimetric and differential thermal analysis (TG-DTA) joint application equipment (SETSYS-18, SETARAM) was used to detect the chemical changes of the composite powders and oxidation resistance of the coated specimens. The theoretical calculation software FactSage was used for calculating the theoretical of phase diagrams and reactions of the composite powders. The surface and cross-sectional morphologies of samples were observed using the scanning electron microscopy (SEM, Hitachi S-3400N, Bruker). The phase composition of cermet coatings was studied by Bruker D2 PHASER powder diffractometer with Cu-Kα radiation (λ = 0.15406 nm) operated at 40 kV and 200 mA.

3. Results and Discussions

3.1. Sintering Temperature of Coatings
In order to determine the appropriate sintering temperature of NiCr/WC cermet coatings, TG-DTA curves of the substrate, the Ni+Cr+WC and Ni+Cr+WC+ZrB₂ composite powders from 600 °C to 1400 °C in Ar were meticulously carried out. The results of different samples mentioned above are shown in figure 1 and correspond curve 1, curve 2 and curve 3, respectively. In figure 1, it is obvious that there is little change in all TG curves during continuous heating, while the endothermic peak existed in various DTA curve has a big difference. From curve 1 of DTA, the initial softening temperature (T₁) of nickel-base alloys substrate is detected about 1260°C. Therefore, the sintering temperature of all candidate cermet coatings should lower than T₁ in order to protect the Ni-based
substrate.

The endothermic peak existed in DTA of curve 2 is at 1343 °C, which is the sintering temperature of the NiCr/WC cermet coating. The sintering temperature is above T_s evidently. When using the ZrB_2 as additive, according to the endothermic peaks existed in DTA of curve 3, the sintering temperature of the cermet coating is 1162 °C or 1220 °C, which is obviously lower than 1260 °C. Comparing with the sintering temperature of the composite powders without ZrB_2, the eutectic point of the NiCr alloy of ones with adding ZrB_2 is apparent lower and the value of sintering temperature has been reduced about 121 °C at least, indicating that the ZrB_2 has sintering-aid effect. Overall, experiments have confirmed that the sintering temperature of the NiCr/WC cermet coating with ZrB_2 additive is 1220 °C rather than 1343 °C.

Figure 1. TG-DTA curves of the composite powders and substrate raising up to 1400 °C in argon: curve 1 substrate, curve 2 Ni+Cr+WC, curve 3 Ni+Cr+WC+ZrB_2.

3.2. Microstructure of Coatings

The NiCr/WC cermet coatings were sintered on the surface of nickel-base alloy at 1220 °C for 10 min. The surface and cross-sectional morphologies of different coatings are displayed in figure 2. Figure 2a and 2c show the surface and cross-sectional morphologies of coatings without ZrB_2. It is obvious that a large number of holes and pores appear on the structure of the coating. However, with the introduction of ZrB_2, those holes and pores in microstructure of coating nearly disappear as shown in figures 2b and 2d, which implies the dense cermet has been successfully obtained.

Figure 2. Surface morphologies of the cermet coating: (a) without additives, (b) add ZrB_2; Cross-sectional morphologies of the cermet coating: (c) without additives, (d) add ZrB_2.
3.3. Densification Mechanism of Coatings

To illustrate the reason of ZrB<sub>2</sub> additive could reduce the sintering temperature of NiCr/WC cermet coatings, the binary and multi-component phase diagrams were calculated by using the FactSage. The different calculation results of WC-ZrB<sub>2</sub>, Cr-ZrB<sub>2</sub> and Ni-ZrB<sub>2</sub> phase diagrams are shown in figure 3. In all phase diagrams, the regions of liquid phases existed are marking out with red. And the minimum temperature of the liquid phase existed (T<sub>l</sub>) in WC-ZrB<sub>2</sub>, Cr-ZrB<sub>2</sub> or Ni-ZrB<sub>2</sub> binary component phase system is 2110 °C, 1600 °C and 1137 °C, respectively.

![Figure 3](image_url)

**Figure 3.** Theoretical calculation of phase diagrams of the composite powders: (a) WC+ZrB<sub>2</sub>, (b) Cr+ZrB<sub>2</sub>, (c) Ni+ZrB<sub>2</sub>.

The TG-DTA curves of WC-ZrB<sub>2</sub>, Cr-ZrB<sub>2</sub> and Ni-ZrB<sub>2</sub> composite powders from 600 °C to 1300 °C in Ar were also carried out and the results are demonstrated in figure 4. It is worth to note that only in the Ni-ZrB<sub>2</sub> phase diagram, the T<sub>i</sub> (1137 °C) is under the T<sub>s</sub> (1260 °C) of Ni-base alloy, and only in the DTA curve 3 of Ni-ZrB<sub>2</sub> in figure 1, there appear the endothermic peak near 1137 °C. So there emerge the liquid phases in the composite powders simultaneously containing Ni and ZrB<sub>2</sub> when the heat treatment temperature is below 1260 °C. In other words, there is a chemical reaction between Ni and ZrB<sub>2</sub> if the temperature is between 1137 °C and 1260 °C. It can be carried out spontaneously at the temperature range of 1100 °C-1260 °C by the software FactSage as shown in equation (1).

\[
22\text{Ni}+3\text{ZrB}_2 \rightarrow \text{Zr}_2\text{Ni}_{13}\text{B}_6+\text{NiZr}
\]  

(1)

The parameters of thermodynamic criterion of the chemical equation (1) were calculated and shown in table 1, implying the reaction between Ni and ZrB<sub>2</sub> could carry out spontaneously at the temperature range of 1100 °C-1260 °C.

As shown in figure 1, the obvious endothermic peaks of the Ni+Cr+WC+ZrB<sub>2</sub> composite powders are at 1162 °C and 1220 °C. In order to demonstrate further the effect of ZrB<sub>2</sub> in the practical coatings, the theoretical multi-component phase diagrams of two kinds of composite powders at 1162 °C and 1220°C are obtained and shown in figure 5, respectively. The results show that the liquid phase appears only when both Ni and ZrB<sub>2</sub> are implemented in a system as well. Compared with the area of the liquid phase at 1162 °C as showed in figure 5b, as temperatures rise to 1220 °C, the area of the liquid phase becomes larger (figure 5d), which indicates that the categories and quantities of liquid phases are also increasing.

The effects of the liquid phases formed in the coatings during the heating process were carefully concluded as following: (1) wetting WC solid ceramic phase to increase the physical bonding force on the interface between metal binding and ceramic reinforcement phase; (2) squeezing air holes to ensure the dense structure; (3) enhancing the ion diffusion between the substrate and coatings. Overall, the densification mechanism of coatings has been illustrated through the comprehensive analysis of both experimental and theoretical calculation results, and the liquid phase appears only when the Ni and ZrB<sub>2</sub> are all introduced in a system at the temperature between 1100 °C and 1260 °C.
Figure 4. TG-DTA curves of the composite powders and substrate raising up to 1300 °C in argon: (4) WC+ZrB₂, (5) Cr+ZrB₂, (6) Ni+ZrB₂.

Table 1. Thermodynamic data of three kinds of solid state reactions (1), (2) and (3).

| Chemical equation | $T$ (°C) | $\Delta H$ (kJ·mol$^{-1}$) | $\Delta S$ (J·mol$^{-1}$·K$^{-1}$) | $\Delta G$ (kJ·mol$^{-1}$) | Reaction type |
|-------------------|---------|-----------------------------|---------------------------------|---------------------------|---------------|
| (1)               | 1100    | -181.352                    | 27.518                          | -219.414                  | exo           |
|                   | 1260    | -179.876                    | 28.525                          | -223.609                  |               |
| (2)               | 112.860 | 112.860                     | 136.547                         | -91.026                   | endo          |
| (3)               | 1220    | 156.370                     | 255.111                         | -224.550                  | endo          |

Figure 5. Theoretical calculation of phase diagrams of the composite powders at different temperatures 1162 °C and 1220 °C: (a) and (c) Ni+Cr+WC, (b) and (d) Ni+Cr+WC+ZrB₂.
3.4. Oxidation Resistance of Coatings

3.4.1. Oxidation Kinetics. In order to explore the antioxidant ability of the cermet coating added ZrB$_2$, the oxidation resistance test was carried out at the temperature range of 800 °C to 1000 °C in pure oxygen for 4h by using thermogravimetric analysis instrument (TG). The test results of oxidize weight gain curves are fitted with equation (2) and it was processed with logarithm and fitted with least square method shown as figures 6a-6c to obtain the values of k and n, which listed in table 2, corresponding to different temperatures [23].

$$\Delta w = k t^n$$  \hspace{1cm} (2)

where $\Delta w$ (mg·cm$^{-1}$) is the mass gain per unit area, $t$ (s) is the oxidized time, $k$ (mg$^2$·cm$^{-4}$·s$^{-1}$) is the oxidation rate constant, and $n$ is the rate exponent. The values of $n$ during the whole experiment period of temperature is approximate and the mean value is 0.63, which indicates that the parabolic rate law of the oxidation kinetics was obeyed at the temperature range of 800 °C-1000 °C. The relationship between the oxidation rate constant $k$ and the oxidation temperatures was in accordance with the Arrhenius equation. The relationship between In$k$ and $1/T$ shown in figure 6d and the activation energy figured out is 103 kJ·mol$^{-1}$ in the range of 800 °C-1000 °C. Compared to the values reported by M. Jafari et al. (WC-12Co coating: 104 kJ·mol$^{-1}$; WC-10Co-4Cr coating: 121 kJ·mol$^{-1}$) and by Gu et al. (NiCrAlY coating: 140 kJ·mol$^{-1}$), the activation energy of NiCr/WC coating added ZrB$_2$ (103 kJ·mol-1) is close to other researches [24, 25].

![Figure 6](image-url)

**Figure 6.** Kinetic curves of cermet coatings added ZrB$_2$ oxidized at different temperatures in pure oxygen for 4 h: (a) $\Delta w/t$ (mg·cm$^{-2}$/s); (b) In$k$/T$^{-1}$. 
Table 2. Summary of the oxidation kinetics parameters of cermet coating added ZrB₂ in pure oxygen at different temperatures: 800 °C, 900 °C, 1000 °C.

| Temperature (°C) | n     | k (mg²·cm⁻⁴·s⁻¹) |
|------------------|-------|------------------|
| 800              | 0.5699| 3.20×10⁻⁴        |
| 900              | 0.6578| 8.97×10⁻⁴        |
| 1000             | 0.6761| 1.95×10⁻³        |
| Activation energy (kJ·mol⁻¹) | 103       |

3.4.2. Carbide in Coatings. The cross-sectional morphologies of oxidized cermet coating added ZrB₂ is displayed in figure 7. It is obvious that oxidation occurs only on the surface of the coating and it plays a good protective role for substrate. And it is indicated that (1) it can be seen from the oxidation depth of the coating that the coating plays a role in preventing the substrate from being oxidized; (2) the oxidation reaction mainly occurred around the WC particles. Therefore, it is discussed from the structure of carbide in cermet coatings to explore the cause of high oxidation barrier.

![Cross-sectional morphologies of the cermet coatings added ZrB₂ oxidized in pure oxygen atmosphere at 1000 °C for 4 h.](image)

To discuss carbide in coatings, the distribution region of carbide (WC, CrₓCᵧ) in the Ni+Cr+WC+ZrB₂ theoretical calculation multi-component phase diagrams at 1220 °C were calculated by using the software FactSage and it is shown as figure 8a coloured with different colours. The following two kinds of solid state reactions (3) and (4) may occur at 1220 °C.

\[7\text{Cr}+6\text{WC}\rightarrow\text{Cr}_7\text{C}_3+3\text{W}_2\text{C} \quad (3)\]
\[23\text{Cr}+12\text{WC}\rightarrow\text{Cr}_{23}\text{C}_5+6\text{W}_2\text{C} \quad (4)\]

According to the thermodynamic criterion of \( \Delta G=\Delta H-T\Delta S<0 \), the calculation results (table 2) show that two kinds of solid state reaction (3) and (4) can occur at 1220 °C. Reaction (1) is exothermic reaction and the reaction (3) and (4) are endothermic reaction. The results shown that the endothermic and exothermic reactions occur at the same time and resulted in the cover up of the peaks. And it gives one of reasons that there are no exothermic peaks in the TG-DTA curves of the composite powders.

The expected structure of the WC particle is shown in figure 8b. It is shown that the surface of the WC particles is coated by CrₓCᵧ and surrounded by NiCr alloy. Between the ceramic reinforced phase WC and metal bonding phase NiCr alloy formed chemical metallurgy combination layer and physical wetting layer to improve the phase interface binding force. Chromium carbides in coatings were detected by XRD (figure 8c) analysis. Namely, it is in good agreement with the calculated results.

Comprehensive analysis and results indicate that, the oxidation behaviour mainly happened to the carbide exposed on the surface in the initial stages of oxidation. There are two characteristics of the WC particles in the internal structure of cermet coating. On the one hand, the WC particles was wetted...
by Ni or Cr to increase the physical bonding force on the interface between metal binding and ceramic reinforcement phase when the liquid phases generated at 1220 °C. On the other hand, it coated by CrxCy resulted from the active reaction between Cr and WC. With the increase of oxidation time, the oxidation of NiCr alloy has been increased and generated metallic oxide to slow down the total oxidation rate.

Figure 8. (a) Theoretical calculation of distribution region of carbide (W,Cy, Cr,Cx) of Ni+Cr+WC+ZrB2 composite powders at 1220 °C in phase diagrams; (b) The new form of WC particle in coatings; (c) Cr,Cx in the XRD patterns of Ni+Cr+WC+ZrB2 composite powders at 1220 °C.

4. Conclusions

This study aimed to explore the densification mechanism and high temperature oxidation kinetic of vacuum-melted NiCr/WC cermet coatings by adding ZrB2. By theoretical and experimental analysis, the main conclusions can be summarized as follows:

1) The densification mechanism of NiCr/WC cermet coating added ZrB2 is mainly attributed to the reaction between Ni and ZrB2 and the liquid phases formed at 1220 °C.

2) The surface of the WC particles is coated by Cr,Cx and surrounded by NiCr alloy. Chromium and nickel oxide thin layers possessed barrier effect for oxygen to prevent oxidation of WC under the conditions of high temperature oxidation.

References

[1] Kim I S, Choi B G, Hong H U, Do J and Jo C Y 2014 Mater. Sci. Eng. A 593 55
[2] Zeng Z, Kuroda S and Era H 2009 Surf. Coat. Technol. 204 69
[3] Hemker K J, Mendis B G and Eberl 2008 Mater. Sci. Eng. A 483-484 727
[4] Kim D, Jang C and Ryu W S 2009 Oxid. Met. 71 271
[5] Wu Y S, Qiu W Q, Yu H Y, Zhong X C, Liu Z W, Zeng D C and Li S Z 2011 Appl. Surf. Sci. 257 10224
[6] Niranatumpoon P and Koiprasert H 2011 Surf. Coat. Technol. 206 440
[7] Musil J and Fiala J 1992 Surf. Coat. Technol. 52 211
[8] Liu S and Zhang W 2005 J. Alloys Compd. 391 146
[9] Shen D, Li M, Gu W, Wang Y, Xing G, Yu B, Cao G and Nash P 2009 J. Mater. Process. Technol. 209 2676-2680
[10] Liu D, Hu P and Min G 2015 Optics & Laser Technology 69 180
[11] Jacobs L, Hyland M M and Bonte M D 1999 J. Therm. Spray Technol. 8 125
[12] Liao H, Normand B and Coddet C 2000 Surf. Coat. Technol. 124 235
[13] Wu Q and Li W 2011 Materials Transactions 52 560
[14] Cho J E, Hwang S Y and Kim K Y 2006 Surf. Coat. Technol. 200 2653
[15] Huang X, Sun Q and Fan K 2006 Conference on Nano/Micro Engineered and Molecular Systems 18-21 1060
[16] Zhao Y J, Zheng Y and Zhou W 2014 *Int. J. Refract Met. H.* **46** 20
[17] Wang J Y, Ni X H and Yang Q Z 2003 *Int. J. of Plant Engineering and Management* **8** 60
[18] Ren X H, Yu L M, Liu Y C, Li H J, Wu J F and Liu Z H 2016 *Int. J. Refract Met. H.* **61** 207
[19] Miao L, Wang Y N and Li Y H 2013 *Advanced Materials Research* **750-752** 2052
[20] Wang Y N, Han L Y and Wang X D 2010 *Advanced Materials Research* **154-155** 942
[21] Xuan T P, Min D and Huo Y 2005 *Tribology* **25** 102
[22] Pang X X, Liu P C, Liu T T, Li Q, Wang Q F and Zhang P C 2014 *J. of Function Materials* **45** 44
[23] Kou J and Le J 2015 *Oxid. Met.* **84** 21
[24] Jafari M, Enayati M H, Salehi M and Nahvi M 2013 *Int. J. Refract Met. H.* **41** 78
[25] Gu L J, Zou B L, Fan X Z, Zeng S B, Chen X L, Wang Y and Cao X Q 2012 *Corrosion Science* **55** 164