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Influence of Processing Parameters on the Microstructure and Oxidation Behavior of Hot Pressed Ni-20Cr + WC Metal Matrix Composites

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Abstract. Ni20Cr+WC composites with a gradient in the volume fraction of hard WC particles are ideal materials for applications where high temperature oxidation and erosion resistance are desired properties. The WC particles impart erosion resistant and the Cr content of the alloy, oxidation resistance. This paper presents the influence of WC particle content and consequently the extent of densification, on the oxidation behavior of hot pressed Ni20Cr+WC composites. Oxidation measurements in the range 700-1000°C revealed overall parabolic behavior. The increase in oxidation rate with WC content has been attributed to formation of islands of WO₃ globules protruding through the Cr₂O₃.

Introduction

Metallic materials for use at high temperatures should be resistant to degradation resulting from reaction with the environment and have adequate mechanical properties. These high temperature materials are usually iron, nickel or cobalt based alloys. These alloys rely on the formation of a continuous and slow growing oxide scale for their protection [1]. On Ni20Cr alloys the characteristics of the surface oxide depend on many factors and includes alloy composition, surface treatment, time and temperature of oxidation as well as oxygen pressure [2]. The oxide formed on Ni20Cr at high temperatures in oxidizing environments consists of an external layer of NiO, an inner layer of NiO with Cr₂O₃ particles and a layer of NiCr₂O₃ or Cr₂O₃ [3,4]. After extended periods of oxidation, a continuous layer of Cr₂O₃ forms along the alloy/oxide interface as the Cr₂O₃ particles coalesce. The growth of this oxide depends essentially on chromium and oxygen diffusion mechanisms through the alloy. At this stage the influence of defects such as voids and grain boundaries is significant as these operate as preferred paths for the transport of chromium and oxygen ions.

The addition of tungsten carbide (WC) particles to Ni20Cr alloy confers high temperature erosion resistance to the composite. WC has very high melting point and hardness. It has been shown that upon exposure of this composite to an oxidizing environment, depending on oxygen pressure and surface temperature, oxygen adsorption takes place and leads to the formation of different compounds on the surface, such as elemental W, WO₃ or WO₂ and carboxides. Also as oxygen reacts with C at high temperatures, CO is liberated [5]. On the other hand, formation of WO₃ and complex oxides based on (Ni)WO₄ has been observed on WC-16%Ni alloys in the temperature range 500-800°C [6].

This paper therefore addresses the oxidation behavior of hot pressed Ni20Cr+WC composites in the temperature range 700-1000°C and discusses the influence of processing parameters.

Methods and Materials

Ni20Cr+WC composites were made using gas atomized Ni20Cr powder with average particle size of 53 μ m (Fig. 1) and WC powder with average particle size of 8 μ m (Fig. 2). The specimens were compacted and sintered in a hot press with a graphite matrix and under the following conditions: 10°C /min heating rate, 30 minutes at the temperature, and 20 MPa argon atmosphere. Composites with 0, 5, 10 and 20 volume% WC were prepared (Fig. 3-6). The composites were cut into smaller specimens 2x2x2 mm in a low velocity Isomet cutter. The specimens were ground to 600# mesh, degreased ultrasonically in acetone and dried in an oven before their surface areas were measured to a precision of $\pm 1\mu$ m. Isothermal oxidation measurements were carried out at 700 to 1000°C in a Shimadzu 50H thermogravimetric analyzer in synthetic air (flow rate of 15mL/min). A scanning electron microscope coupled to an EDS system was used to examine the specimen surfaces.

Results and Discussion

Table I presents the densification results of the composites taking as basis the densities of WC (15.6 g/cm³) and the Ni20Cr alloy (8.3 g/cm³).

Fig. 7-12 reveal the morphology of the surface oxides on the Ni20Cr+5%WC composite specimens oxidized at various temperatures. The uniform layer on the surface is Cr₂O₃. This oxide cracks and spalls as the tungsten oxide forms on the WC particles. The WC particles are often agglomerates between Ni20Cr particles. The size of globules [7] on the surface increase with increase in oxidation temperature. During oxidation of these composites, Cr₂O₃ forms on the Ni20Cr and tungsten oxide on the WC agglomerates. The mass change per unit area as a function of time at various temperatures are shown in Fig. 13(a) and (b) for the composites containing 5% and 10%WC respectively. Overall, parabolic oxidation behavior can be observed for the two types of composites oxidized at the different temperatures. Similar oxidation curves were obtained for the composites with the higher amounts of WC, and the overall mass gains were significantly higher for those with higher WC contents. Table 1 shows the extent of densification of the composites and it decreases with increase in WC content. This indicates an increase in the number of discontinuities on the composite surface with increase in WC, mainly at Ni20Cr-WC interfaces. These discontinuities are preferred sites for growth of Cr₂O₃ and WO₃, due to easy access of oxygen followed by formation of Cr₂O₃ at the Ni20Cr/Ni20Cr particle interfaces and the formation of voluminous WO₃ at WC/Ni20Cr interfaces. The formation and growth of these oxides is indicated by the marked increase in mass during oxidation with reduction in densification of the composites.

Table 1. Density and extent of densification (%) of the Ni20Cr+WC composites.

Composite	Theoretical Density (g/cm ³)	Density (g/cm ³)	Densification (%)
Ni20Cr	8.30	7.54	90.89
Ni20Cr+5%WC	8.67	7.59	87.61
Ni20Cr+10%WC	9.03	7.51	83.13
Ni20Cr+20%WC	10.86	7.25	74.26

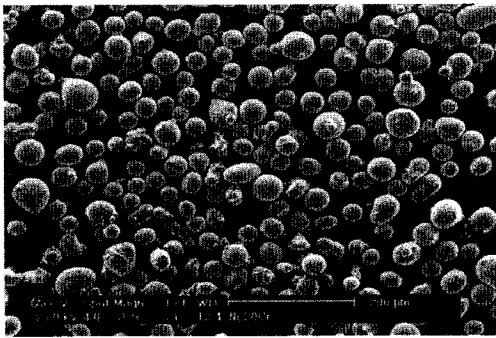


Fig. 1. Morphology of Ni20Cr powder.



Fig. 2. Morphology of WC powder.

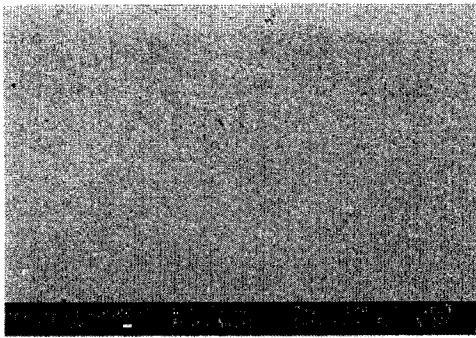


Fig. 3. Cross-section of Ni20Cr alloy.

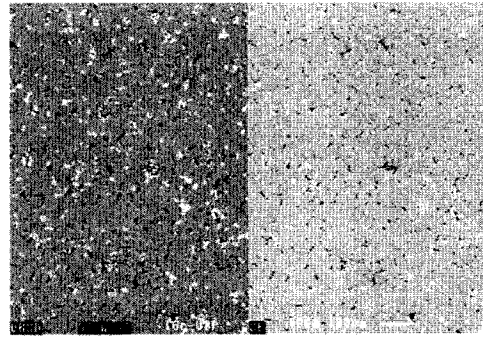


Fig. 4. Cross-section of Ni20Cr+5%WC composite.

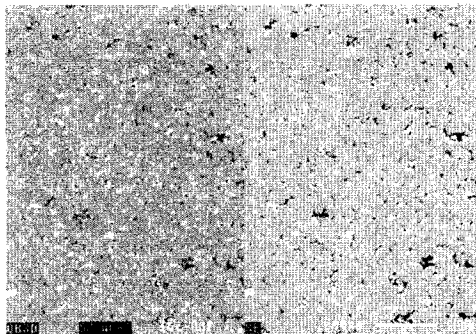


Fig. 5. Cross-section of Ni20Cr+10%WC composite.

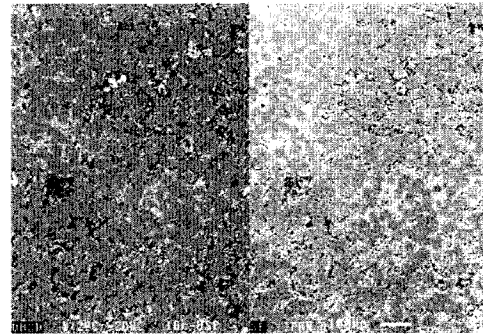


Fig. 6. Cross-section of Ni20Cr+20%WC composite.

The oxidation behavior at the different temperatures are similar. Parabolic growth rates are observed characteristic of diffusion controlled oxidation processes. At temperatures above 950°C, the reduction in the overall mass change with time at temperature can be attributed to further oxidation of Cr_2O_3 to form volatile CrO_3 [8].

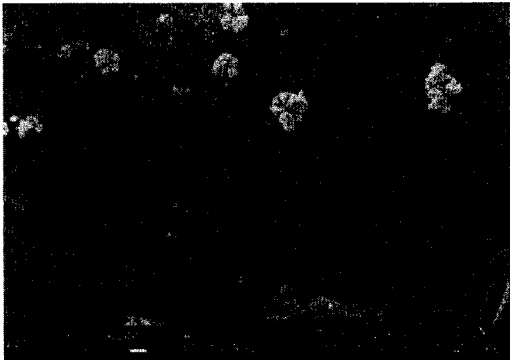


Fig. 7. Ni20Cr+5%WC oxidized at 700°C.

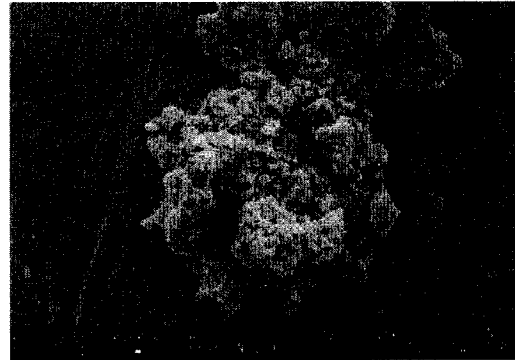


Fig. 8. Ni20Cr+5%WC oxidized at 750°C.



Fig. 9. Ni20Cr+5%WC oxidized at 800°C.

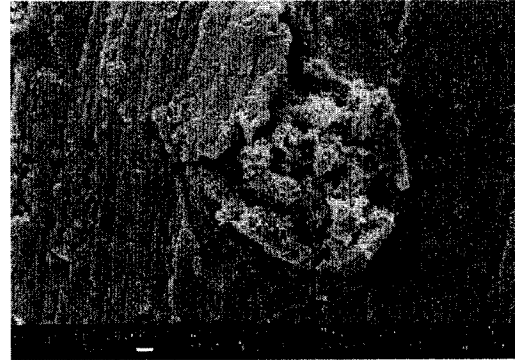


Fig. 10. Ni20Cr+5%WC oxidized at 850°C.

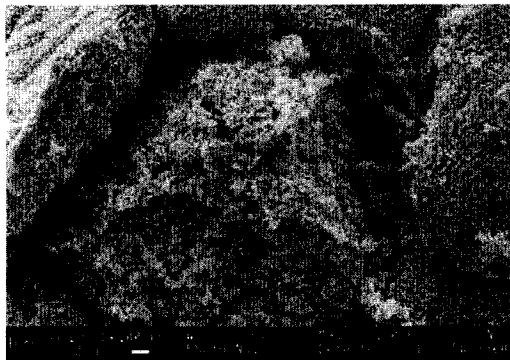


Fig. 11. Ni20Cr+5%WC oxidized at 900°C

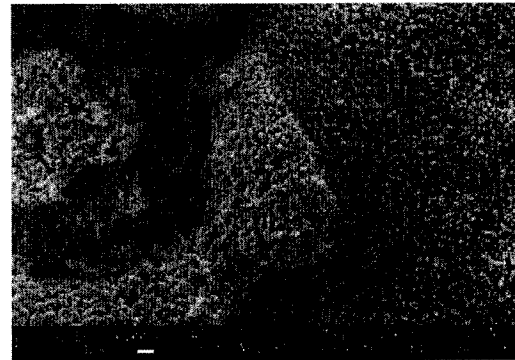


Fig. 12. Ni20Cr+5%WC oxidized at 950°C

Fig. 14 shows the mass change after 300 minutes for the various composites as a function of temperature. The curve corresponding to Ni20Cr alloy reveals a steady increase in mass with temperature and reaches a maximum at 950°C. With addition of and increase in WC content of the composite, the mass changes are significantly higher with temperature and the peak of these curves are observed at lower temperatures with increasing WC. The peak mass gain for the composite with 5%WC is at 900°C, for that with 10%WC at 850°C and for that with 20%WC below 700°C. These peaks in the mass gain in Fig. 14 at lower temperatures with increasing WC in

the composite is directly attributable to the decrease in densification of the composite, consequent increase in the number of surface discontinuities and to increase in WC agglomerate islands. The decrease in mass following the peak for the different composites can be attributed to spalling of the oxide globules and formation of volatile CrO_3 at the higher temperatures.

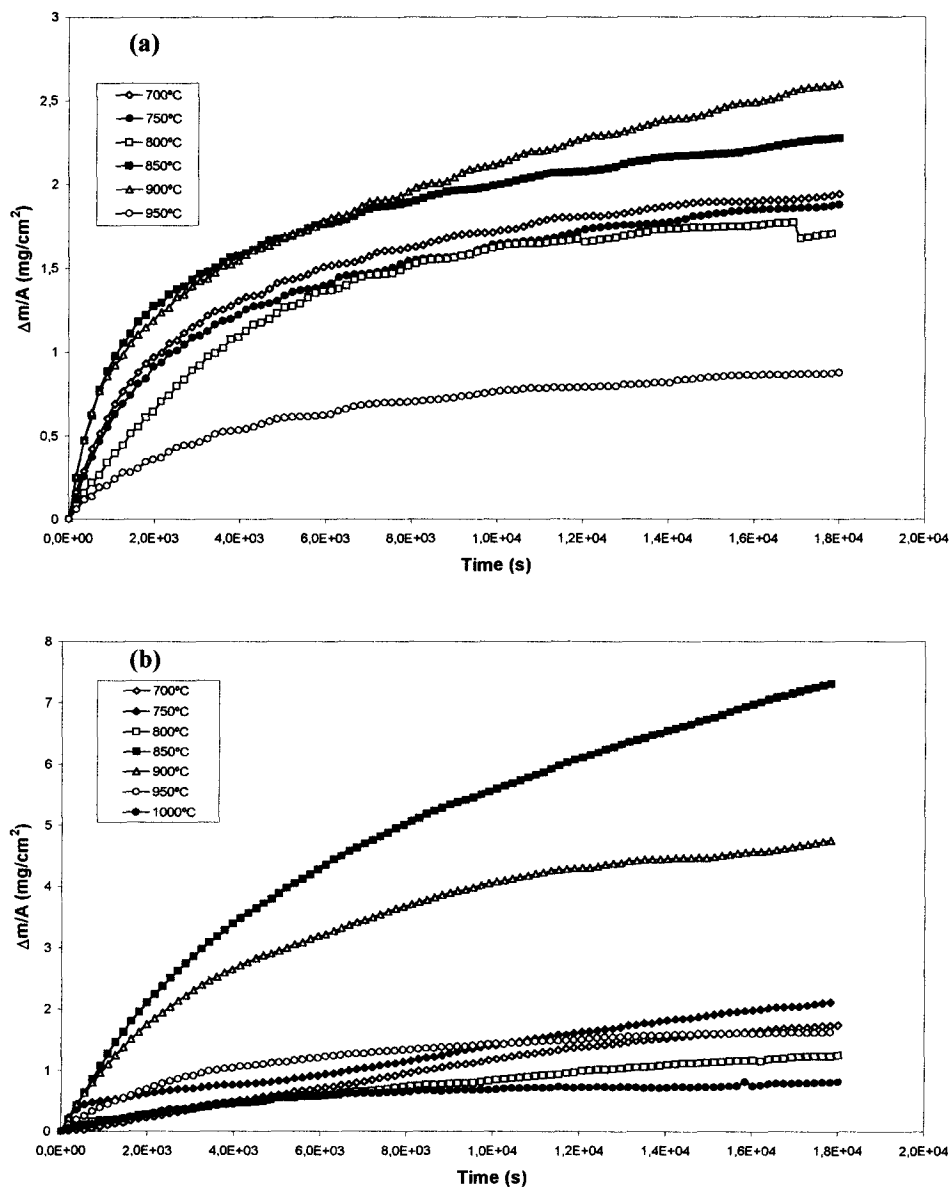


Fig. 13. Mass gain per unit area as a function of oxidation time for the composites (a) $\text{Ni}_{20}\text{Cr}+5\%\text{WC}$ and (b) $\text{Ni}_{20}\text{Cr}+10\%\text{WC}$.

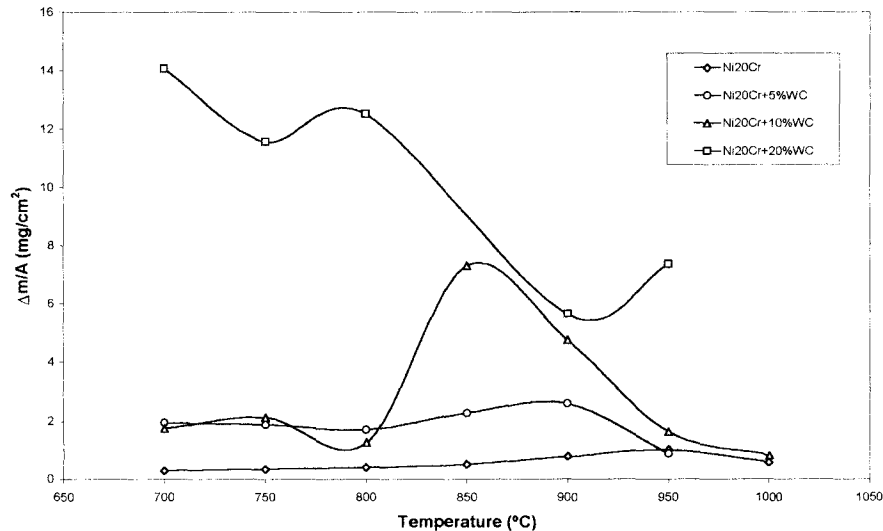


Fig. 14. Mass gain per unit area as a function of oxidation temperature for different Ni20Cr+WC composites.

Conclusions

- Oxidation of the Ni20Cr+WC composites results in formation of Cr_2O_3 and WO_3 . These two oxides grow on the Ni20Cr alloy and on the WC particle agglomerates;
- The mass gain of the Ni20Cr alloy is uniform with time and temperature up to 950°C;
- Increase in the WC content of the composites results in marked increase in oxidation rate and reaches a maximum;
- The peak in the mass gain versus temperature curves of composites oxidized for 300 minutes decreases with increase in WC content and this can be attributed to increase in surface discontinuities and to spalling of WO_3 .

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