

Kinetics of oxidation of Cr_3B_4 cermets cemented by different metallic binders Part 2. Using cobalt and nickel as binders

M.A. El Masry, S.S. Younis, A.M. Khater, A.N. Mahdy and M.F. Abadir

Faculty of Engineering, Cairo University, Giza (Egypt)

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Abstract

Experimental work was carried out to study the effect of process variables on the mechanism of oxidation of Cr_3B_4 in air. Nickel and cobalt were used as metallic binders with weight percentages ranging from 1% to 20%. The experiments covered a temperature range from 400 to 1000 °C and time periods of up to 5 hours. It was found that the use of nickel as a binder gave the best results as it improves the thermal stability of chrome boride cermets at 8 wt.% Ni or more. The mechanism of the oxidation and the rate-controlling steps were determined. In addition, the activation energies for the initial oxidation were calculated. In general, increasing the binder content, increased the thermal stability.

INTRODUCTION

Metal binders are added to Cr_3B_4 to introduce some ductility to this brittle material. The effect of iron binder on the oxidation of Cr_3B_4 cermets has been investigated in Part 1 of this study [1]. The aim of the present part is to elucidate the role played by different process variables on the kinetics of oxidation of Cr_3B_4 bonded by nickel and cobalt.

A review of the subject was given in the first part [1].

EXPERIMENTAL

The thermal stability of chrome boride cemented by cobalt and nickel was investigated. Cr_3B_4 and the binder powders were formed into cylindrical compacts by hot pressing. The microstructure before and after oxidation was examined using a scanning electron microscope. The binder content in the compacts varied from 1 to 20 wt.%. The temperature ranged from 400 to 1000 °C in 100 °C steps.

Effect of time and temperature on the oxidation of Cr_3B_4 -Co cermets

The effect of time on the weight gain per unit area, w ($mg\ cm^{-2}$), of 1 wt.% Co and 99 wt.% Cr_3B_4 compacts at different temperatures is shown in Fig. 1. A similar pattern of behaviour is shown for other curves for samples with a higher wt.% Co. It is clear from the figure that no weight gain occurs below $500^\circ C$. Increasing the oxidation temperature, increases the weight gain per unit area. At $900^\circ C$, the oxidation resistance rises markedly. This same behaviour has been encountered in the case of iron binder [1].

Effect of binder content on the oxidation of Cr_3B_4 -Co cermets

The effect of the weight percentage of Co on Δw was studied at temperatures ranging from 500 to $1000^\circ C$. Figures 2 and 3 show the curves corresponding to $500^\circ C$ and $1000^\circ C$ respectively. It is observed from these curves that the stability towards oxidation increases with increasing wt.% of cobalt. At $500^\circ C$, pellets containing more than 4% Co did not oxidise, while at $1000^\circ C$, slight oxidation was observed with up to 8% binder content.

Effect of temperature on the maximum weight gain

This effect is the same for all curves and is shown in Fig. 4. An unexpected behaviour that was also seen with iron binder [1], was observed at $900^\circ C$, where the maximum weight gain is much lower than was expected.

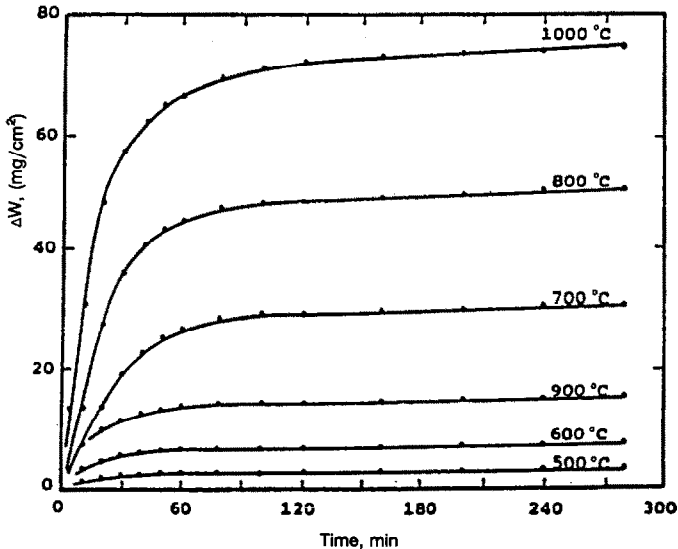


Fig. 1. Kinetic oxidation curves for Cr_3B_4 -1 wt.% Co at different temperatures.

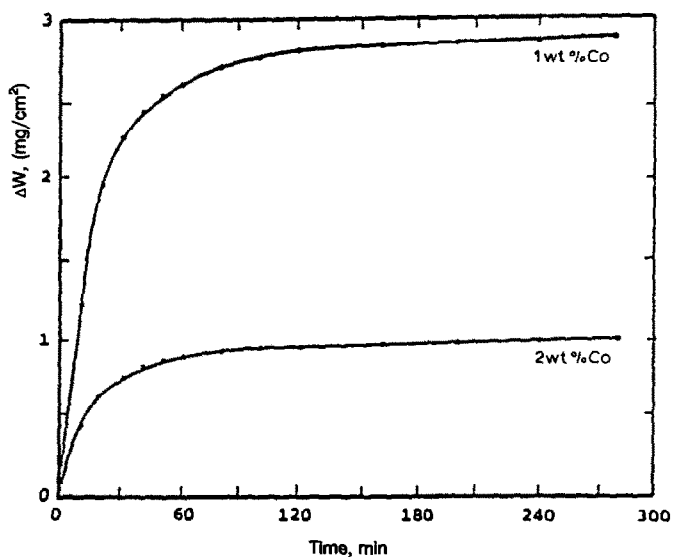


Fig. 2. Isothermal oxidation curves for Cr_3B_4 with 1 and 2 wt.% Co at 500°C in air.

Effect of binder content on the maximum weight gain

Figure 5 illustrates this effect; the maximum weight gain per unit area decreases with increasing weight percent cobalt. Also, it is clear from the figure that the maximum weight gain increases with temperature. High oxidation stability is obtained at a level of 8% Co regardless of oxidation temperature.

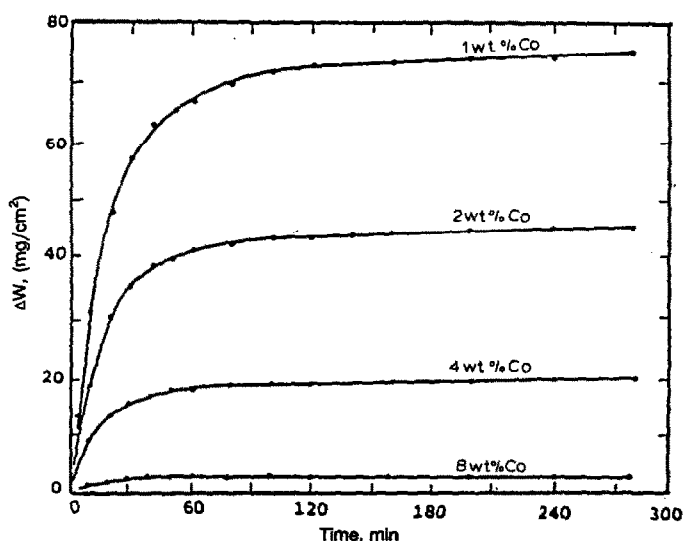


Fig. 3. Isothermal oxidation curves for Cr_3B_4 with 1–8 wt.% Co at 1000°C in air.

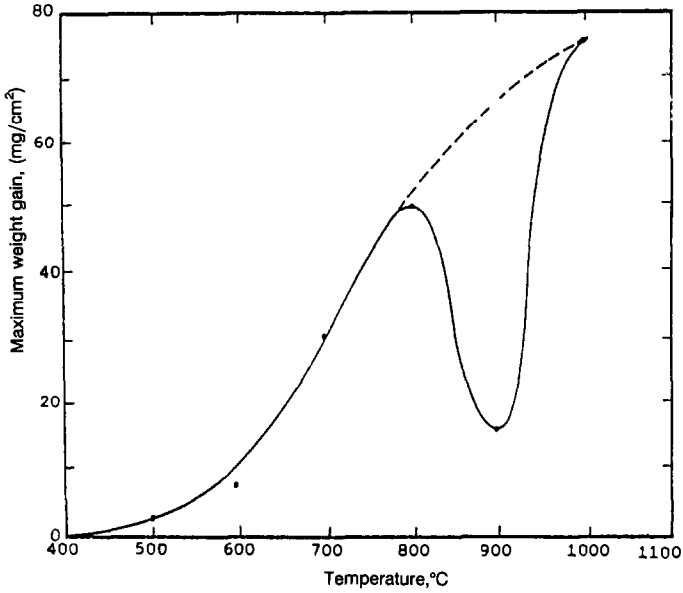


Fig. 4. The effect of temperature on the maximum weight gain of Cr_3B_4 -1 wt.% Co.

Effect of time and temperature on oxidation of Cr_3B_4 -Ni cermets

This effect is shown in Fig. 6. It can be observed that no oxidation occurs below 500 °C; increasing the temperature of oxidation from 500 to 1000 °C

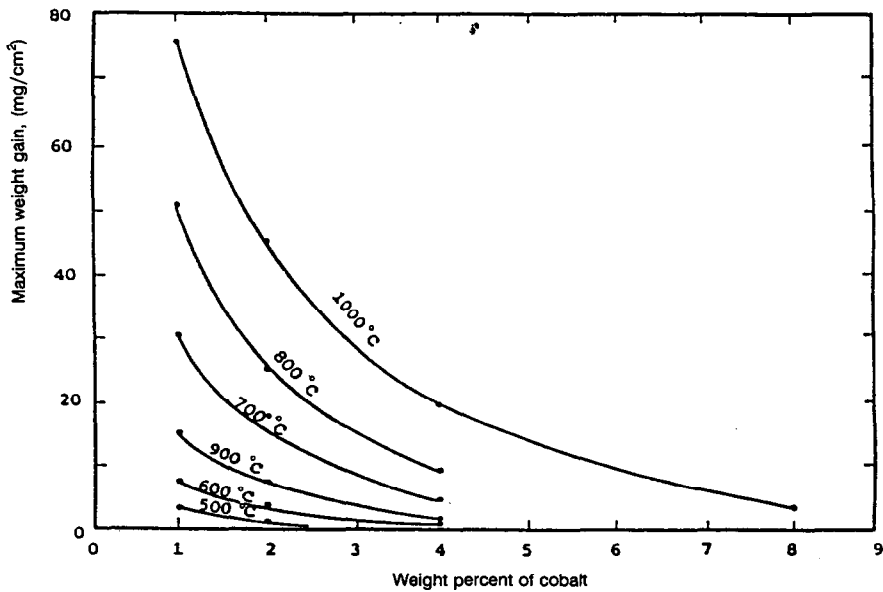


Fig. 5. The effect of cobalt content on maximum gain in weight of Cr_3B_4 -Co cermets at different temperatures.

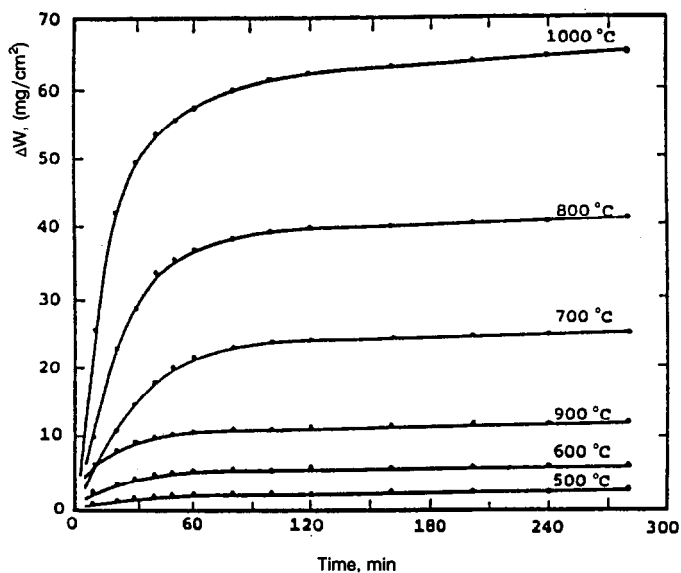


Fig. 6. Kinetic oxidation curves for Cr_3B_4 -1 wt.% Ni at different temperatures.

increases the weight gain per unit area, except at 900°C as was the case with Fe and Co binders. This 900°C anomaly exhibits the pattern shown in Fig. 7. Hence, this phenomenon does not depend on the type of binder used. This peculiar behaviour was interpreted in Part 1 of this work. Comparing

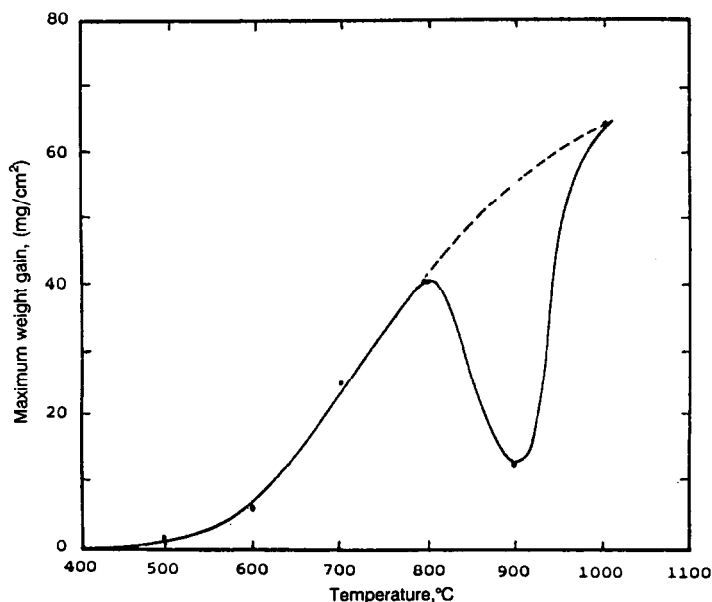


Fig. 7. The effect of temperature on the maximum weight gain of Cr_3B_4 -1 wt.% Ni.

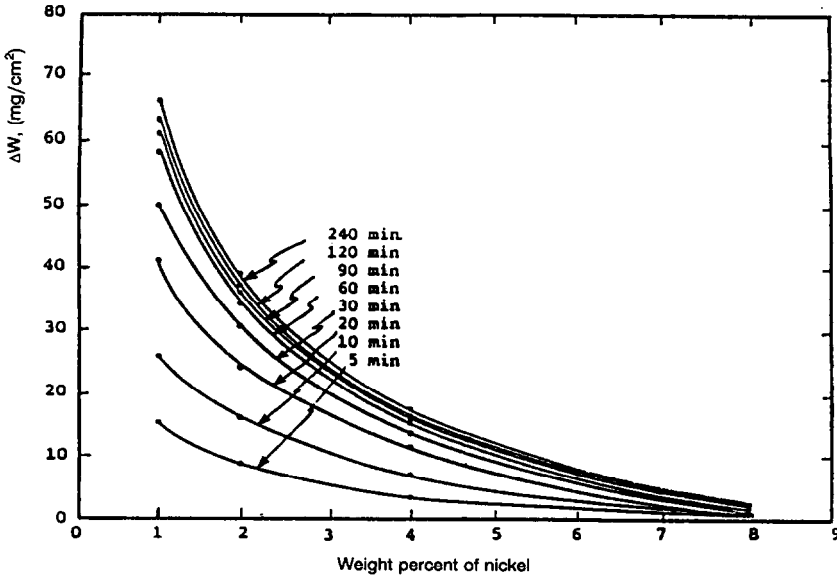


Fig. 8. Weight gain of Cr_3B_4 -Ni cermets at 1000°C and different oxidation times.

the three types of additions, it is seen that addition of 1 wt.% Fe decreased the weight gain from an expected value of 145 mg cm^{-2} to 41 mg cm^{-2} ; in the case of 1 wt.% Co, from 65 to 15 mg cm^{-2} ; and in the case of 1 wt.% Ni, from 55 to 12 mg cm^{-2} .

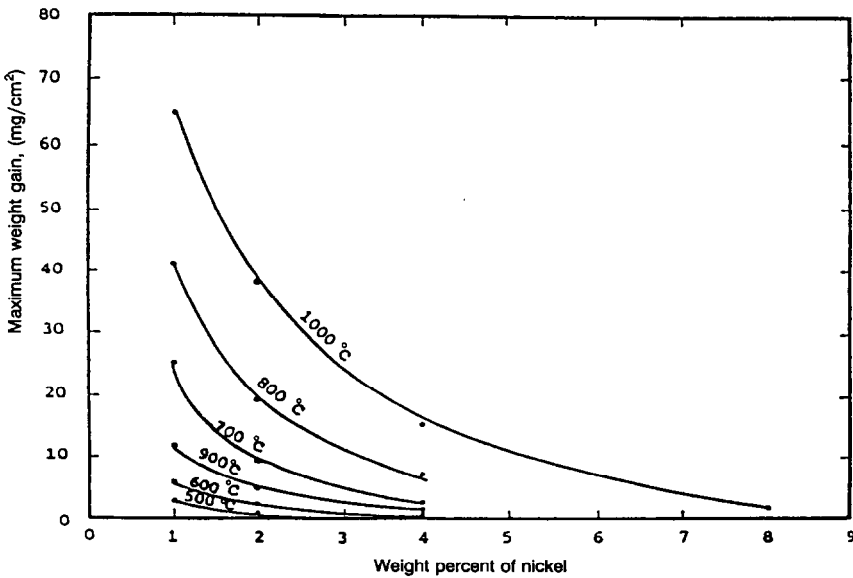


Fig. 9. Effect of cobalt content on maximum gain in weight of Cr_3B_4 -Ni cermets at different temperatures.

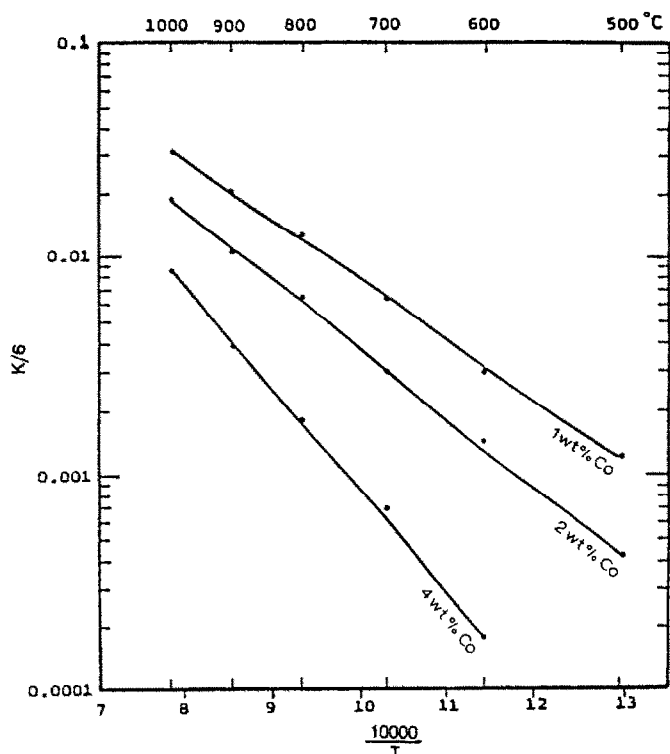


Fig. 10. Rate constant K versus $(1/T \times 10000)$ for Cr_3B_4 -Co cermets at different wt.% of cobalt.

Effect of binder content on oxidation of Cr_3B_4 -Ni cermets

This effect is shown in Fig. 8 where the weight gain at 1000°C after 5, 10, 30, 60, 90, 120 and 240 minutes is plotted. From the figure, it is observed that the weight gain decreases by increasing the binder content, and increases by increasing the oxidation time.

Effect of temperature on the maximum weight gain

This effect is shown in Fig. 9 from which we can observe that the maximum weight gain per unit area decreases by increasing the binder content. Also, the maximum gain increases by increasing the oxidation temperature. At 8% Ni, it is possible to get maximum oxidation resistance regardless of temperature.

Isothermal kinetics of oxidation of compacts

It has been shown that there are three oxidation stages [1]. During the initial stage the rate of oxidation is constant and $dw/dt = K$; the values of the reaction constant K at different temperatures and different weight percent of cobalt and nickel are shown in Figs. 10 and 11. In the next stage, a straight line relationship can be obtained by plotting $f(x)$ against t (see

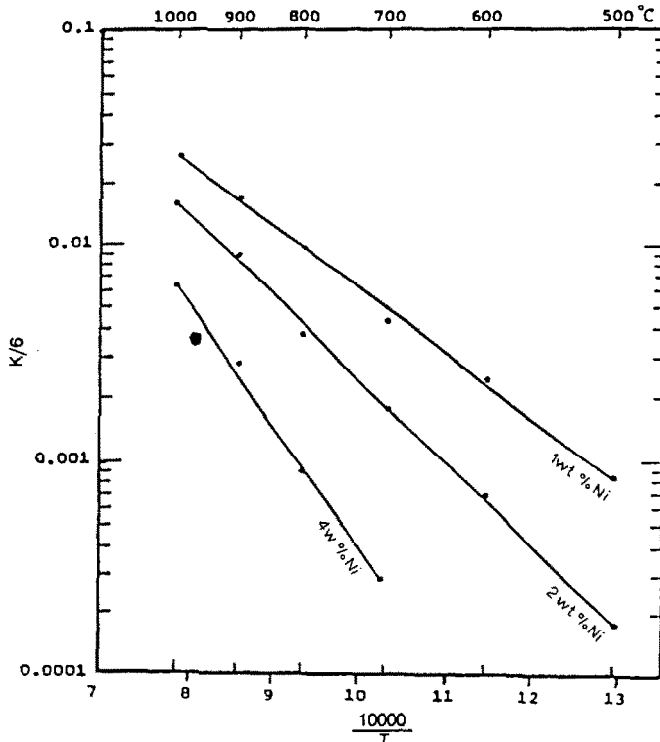


Fig. 11. Rate constant K versus $(1/T \times 10000)$ for Cr_3B_4 -Ni cermets at different wt.% of nickel.

Figs. 12 and 13), where $f(x) = 1 - (1 - x)^{1/2} = K_1 t$. This stage of the oxidation may be considered as a phase-boundary rate-controlling reaction [2].

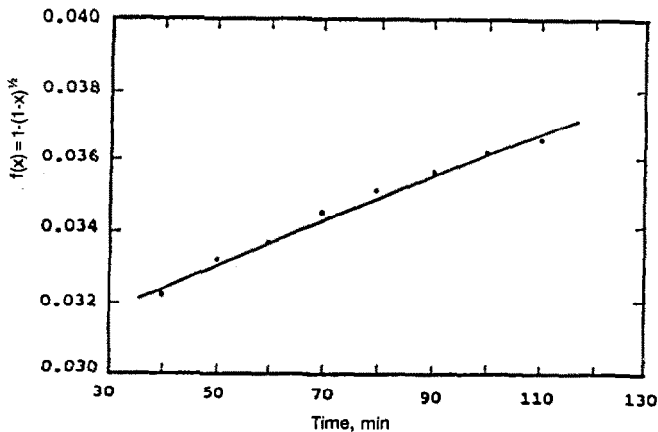


Fig. 12. Intermediate stage of oxidation: $f(x)/t$ relationship assuming phase-boundary motion-controlling for Cr_3B_4 -1 wt.% Co at 1000 °C.

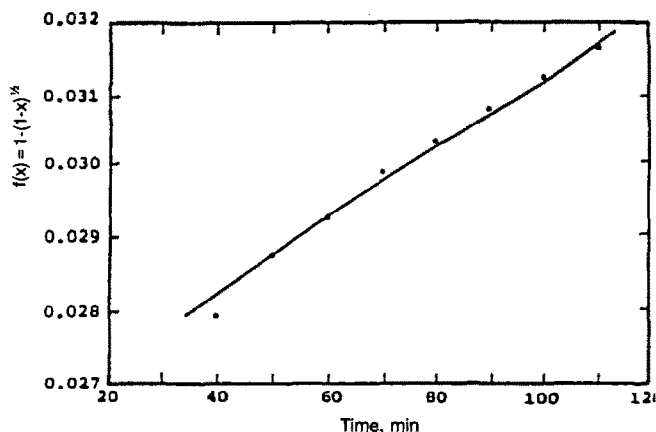


Fig. 13. Intermediate stage of oxidation: $f(x)/t$ relationship assuming phase-boundary motion-controlling for Cr_3B_4 -1 wt.% Ni at 1000°C .

In the final stage of the oxidation, a straight line relation between $f(x)$ and t is obtained when $f(t)$ satisfies the relation $f(x) = (1-x) \ln(1-x) + x = K_2 t$, (see Figs. 14 and 15). This stage is considered as two-dimensional diffusion rate-controlling [2].

Effect of binder content on the reaction constant (K) (initial stage)

This effect is shown in Figs. 16 and 17 which show the relationship between K and the metal content. A logarithmic relation between K and binder content at 1000°C has been obtained: for Cr_3B_4 -Co, $\ln K = -1.2 -$

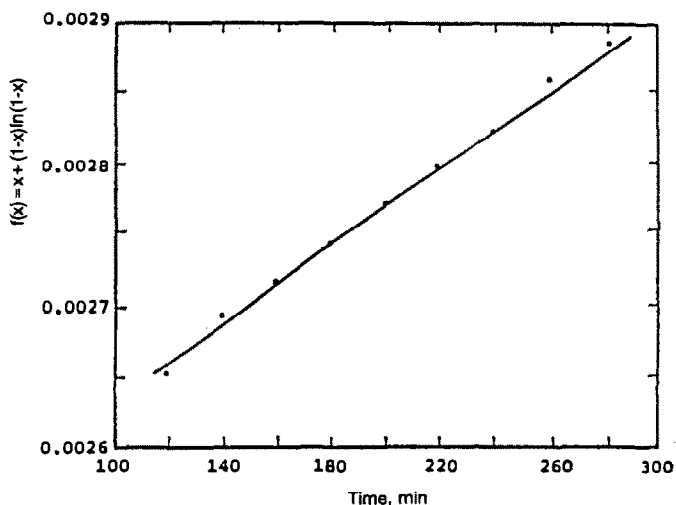


Fig. 14. Final stage of oxidation at 1000°C : $f(x)/t$ relationship assuming two-dimensional diffusion rate-controlling for Cr_3B_4 -1 wt.% Co.

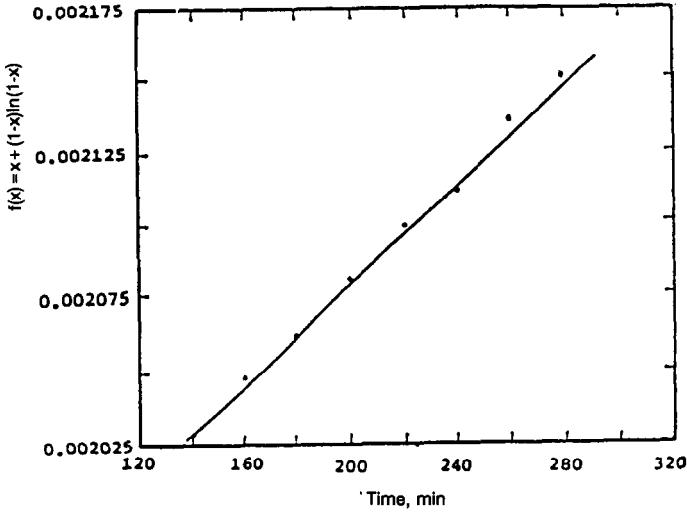


Fig. 15. Final stage of oxidation at 1000°C: $f(x)/t$ relationship assuming two-dimensional diffusion rate-controlling for Cr_3B_4 -1 wt.% Ni.

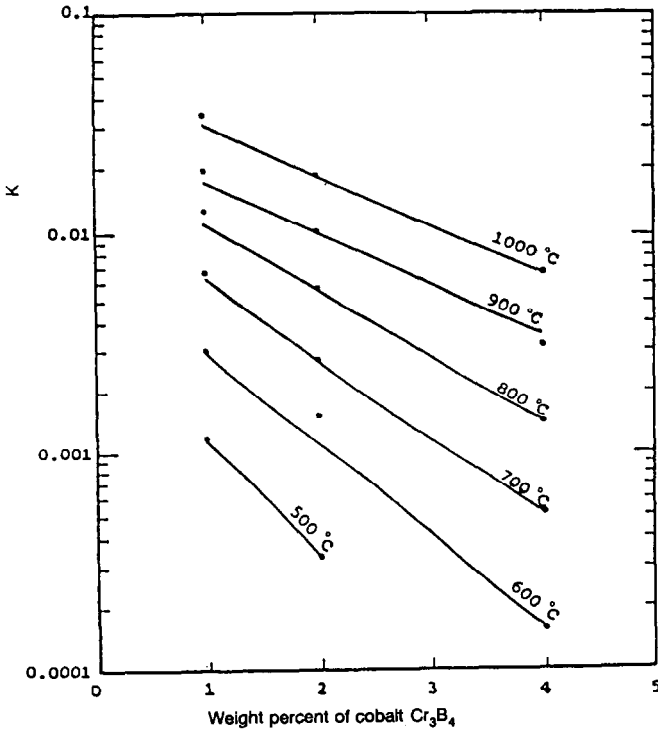


Fig. 16. Rate constant K versus cobalt content.

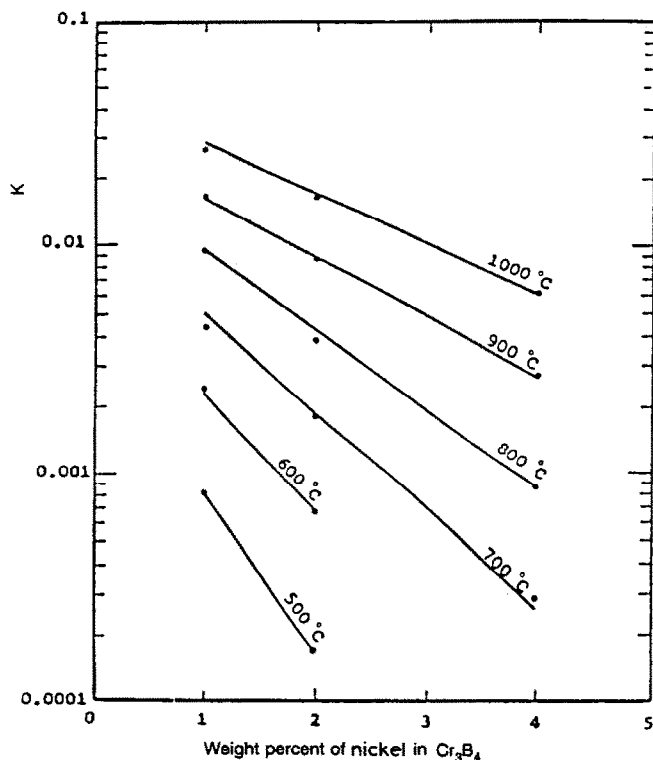


Fig. 17. Rate constant K versus nickel content.

0.4970α ; and for $\text{Cr}_3\text{B}_4\text{-Ni}$, $\ln K = -1.2 - 0.5250\alpha$, where α = weight percent of binder. The corresponding relation for addition of Fe is: $\text{Cr}_3\text{B}_4\text{-Fe}$, $\ln K = -1.2 - 0.1025\alpha$ [1].

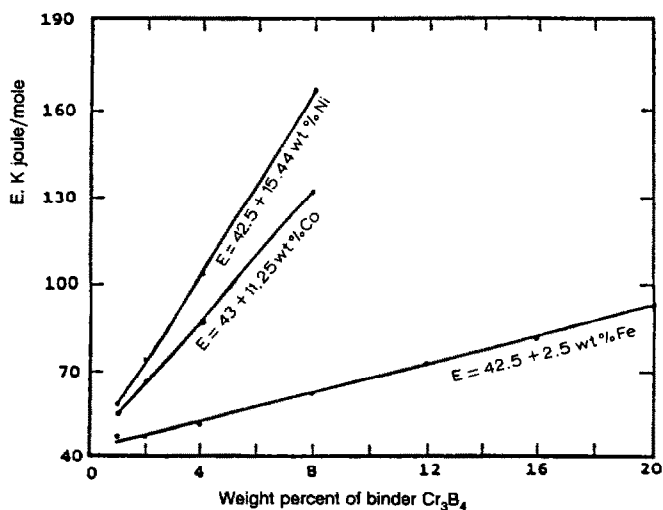


Fig. 18. Activation energy of oxidation for compact with iron, cobalt and nickel binders.

It can be observed that the reaction constants decrease in the order $\text{Cr}_3\text{B}_4\text{-Fe} > \text{Cr}_3\text{B}_4\text{-Co} > \text{Cr}_3\text{B}_4\text{-Ni}$, for the same binder content and oxidation temperature.

Calculation of activation energy during the initial stage of oxidation

It is well known that $K = A \exp(-E/RT)$ and, hence, $\ln K = \ln A - E/RT$. A plot of $\ln K$ against $1/T$ gives a straight line as shown in Figs. 16 and 17. The relationship between the activation energy E and the binder content is shown in Fig. 18. An attempt was made to correlate the increase in E with the increase in binder content. We believe that the metal binder offers a resistance towards the motion of the O^{2-} ions that cause oxidation which increases the activation energy required for oxidation in the initial stage. Using least-squares analysis, the following relationships were obtained: for $\text{Cr}_3\text{B}_4\text{-Co}$, $E = 43.00 + 11.25\alpha$; and for $\text{Cr}_3\text{B}_4\text{-Ni}$, $E = 42.50 + 15.44\alpha$. For $\text{Cr}_3\text{B}_4\text{-Fe}$, $E = 42.50 + 2.5\alpha$ [1]. At $\alpha = 0$, $E = 43 \text{ kJ mol}^{-1}$, which represents oxidation of pure Cr_3B_4 compacts. From these results, we observe that the order of increasing activation energy for the different binders is $\text{Fe} < \text{Co} < \text{Ni}$.

CONCLUSION

The oxidation of chrome boride cermets cemented with metal binders (Fe, Co and Ni) showed that the extent of oxidation increases with temperature, except at 900°C , and decreases with binder content. The binder inhibits the vaporisation of boron and, hence, the decomposition of Cr_3B_4 . The activation energy of the oxidation reaction increases with increasing binder content in the order iron < cobalt < nickel, i.e. among the metallic binders, nickel exhibits the maximum resistance to oxidation.

NOMENCLATURE

A	pre-exponential factor
E	activation energy (kJ mol^{-1})
K	rate constant (first stage of oxidation) (g min^{-1})
R	general gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
t	time (min)
T	temperature (K)
x	conversion
α	wt.% binder
Δw	gain in weight per unit area (mg cm^{-2})

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