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High-temperature oxidation behaviour of base metal elements in nickel-base alloys

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Oxidation of non-precious metals nickel, chromium and copper, nickel-base alloys in an air atmosphere was studied under differential thermal analysis. The results suggest that adding chromium and copper to high-purity nickel metal reduces the amount of oxidation and gives a slower oxidation than in untreated high-purity metals. It is then shown that the activation energy for oxidation in nickel-base alloys is almost the same as that in high-purity nickel metal when alloying elements are added to nickel.

1. Introduction

The parabolic rate law was applied to the oxidation of 80Ni–20Cr alloy observed between 500 and 900° C, and reasonable agreement was found for temperatures above 650° C [1]. For high-temperature oxidation of high-purity nickel between 750 and 1050° C, the parabolic rate law fitted the experimental data well below 900° C, but showed increasing values of the parabolic law constant with time at 900° C and above [2]. The oxidation kinetics in dental Ni–Cr cast alloys agreed with the parabolic rate law in a high-temperature range, 800 to 1010° C [3], showing that test temperature appears to have a stronger influence on oxidation rate than does oxygen partial pressure. In general, chemical bonding between an alloy and porcelain occurs at elevated temperature and in an oxygen-rich environment. Oxidation may take place prior to application of porcelain during a degassing process in dental Ni–Cr alloys. The migration of metallic species occurred by diffusion from alloy to porcelain [4]. In the preferential oxidation, the Ni–Cr alloys were depleted of the more easily oxidized element. As a result, a change in microstructure occurred because of the difference in diffusion rates between various alloying elements [5]. The effect of alloying elements on the thermal behaviour of nickel-base alloys has not been rigorously clarified. This study was undertaken to examine the thermal behaviour of individual alloying elements, as well as that in binary Ni–Cu and Ni–Cr alloys.

2. Materials and methods

The metal powders tested were pure metals such as nickel (99.9% pure), chromium (99% pure), and copper (99.85% pure), all from the Wako Pure Chem. Co., Osaka, Japan, and also nickel-base alloy powders (Fukuda Metal Foil and Powder Co., Kyoto, Japan) which were Ni–14.5Cr alloy (4.28 wt % Si, 2.74 wt % B, 2.71 wt % Fe and 0.69 wt % C) and Ni–7.67Cu alloy (2.21 wt % Si, 1.09 wt % B and 1.19 wt % P), as shown in Figs 1a to e. The metal powders had small particles which were ranged 1 to 30 μm.

Measurement of the oxidation was carried out using thermal analysis equipment (Shimadzu DT-30, Shimadzu Co., Kyoto, Japan). Thermal data were obtained as differential thermal analysis (DTA) as a function of test temperature, and thermogravimetry (TG) as a function of test temperature. Samples (10 mg) for measurements were exposed to an air atmosphere with air flow of 50 ml min^{-1}. Under these measurements, the heating rates were 10, 30 and 50° C min^{-1}, and then the test temperatures were raised from room temperature to 900° C. The oxides were found from the X-ray diffraction pattern, but identification of individual oxides was difficult, because complex phases of the oxide formed with increasing temperature, at high test temperatures. At elevated test temperatures, individual oxides which formed at the surface layers had a complex phase consisting of various oxides inside the specimen [6–9]. Thus the thermal behaviour of alloying elements should be examined at elevated test temperatures. In this study, thermal analysis carried out as above was related to the activation energy for the oxidation of metals and alloy powders.

3. Results

The thermal analysis of the metal powders shown in Fig. 1 was carried out, and DTA and TG curves recorded at three heating rates are shown in Fig. 2. The decrease of DTA curves in Fig. 2a occurs above the temperature indicated as T_t on the DTA curves, i.e. the transition temperature [10, 11]. This temperature indicates that the oxide films tended to exfoliate at lower temperature and that they were adherent at higher temperatures [10, 11].

This transition temperature was also observed for chromium, as shown in Fig. 2b, and the temperatures were detected at heating rates such as 10, 30 and 50° C min^{-1}. From these results, it is seen that the transition temperatures depend on the reaction rate based on the oxidation of pure metals, nickel and chromium. In Fig. 2c, the change of the TG curve with test temperatures for copper and chromium, and their transition

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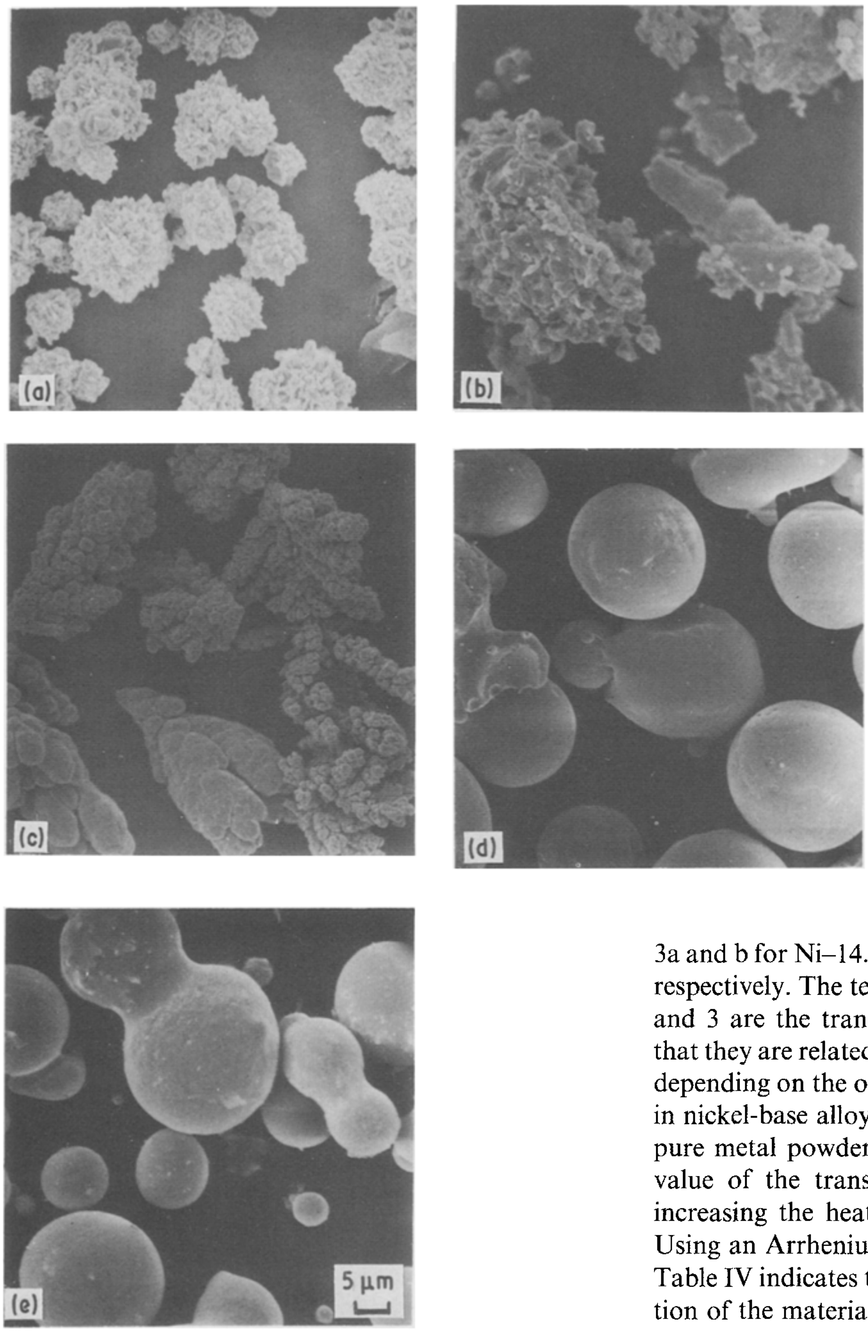


Figure 1 Scanning electron micrographs of the metal powders tested: (a) Ni, (b) Cr, (c) Cu, (d) Ni–14.5Cr, (e) Ni–7.67Cu.

temperatures (T_{t1}, T_{t2} and T_t) may be the temperatures of formation for CuO and Cu_2O, and Cr_2O_3 [6–9], i.e. they occur in the pure copper (bulk specimen) in the ranges 200 to 265 and 520 to 625° C, respectively [8]. In pure chromium, the oxide may be found at a T_t above 400° C [7]. The amount of oxidation at 900° C is indicated in Table I. On increasing the heating rate, the oxidation at 900° C was smaller by about 10% than that at a heating rate of $10° C\,min^{-1}$.

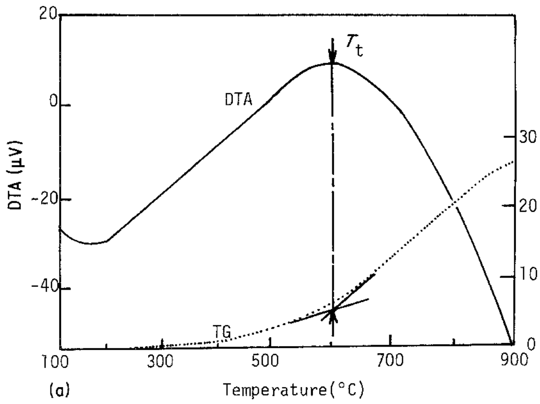
The results of the thermal analysis are shown in Figs 3a and b for Ni–14.5Cr and Ni–7.67Cu alloy powders, respectively. The temperatures indicated at Peaks 1, 2 and 3 are the transition temperatures. It is deduced that they are related to the process of the reaction rate, depending on the oxidation. The amount of oxidation in nickel-base alloy powders was smaller than that in pure metal powders. In Tables II and III, the mean value of the transition temperature increased with increasing the heating rate from 10 to $50° C\,min^{-1}$. Using an Arrhenius plot [1, 3, 12] from these results, Table IV indicates the activation energy for the oxidation of the materials tested. It is seen that the activation energy in alloy powders was almost the same as that of the pure metals nickel, chromium and copper. At the transition temperatures, the activation energy for oxidation in the nickel-base alloy powders increased, with the transition temperature of Peak 1. The nickel-base alloy powders with chromium and copper added to the pure nickel limits the formation of oxide, compared with the larger amount of oxidation of the pure metal.

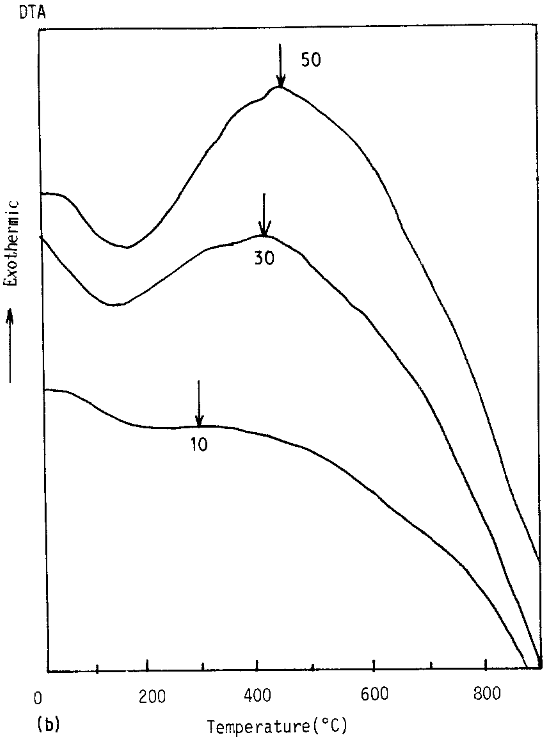
TABLE I Degree of oxidation on increasing the test temperature from room temperature to 900° C at a heating rate of $10° C\,min^{-1}$

Materials	Δm at 900° C (%)
Ni	29.0 ± 0.4
Cr	11.1 ± 0.4
Cu	28.0 ± 0.9
Ni–14.5Cr	0.0
Ni–7.67Cu	1.5 ± 0.1

4. Discussion

Oxidation in the temperature range room temperature to 900° C was attempted for high-purity nickel, chromium and copper metal powders and the Ni–14.5Cr and Ni–7.67Cu alloy powders (Figs 1a to e). Powders having a larger surface area than the bulk specimens were selected in this study because of the very small amount of oxidation. Their metal powders indicated changes of the DTA curve with the increase of the TG curve with increasing test temperature (Fig. 2). The amount of oxidation in pure metal powders was, as given in Table I, larger than that in nickel-base alloy





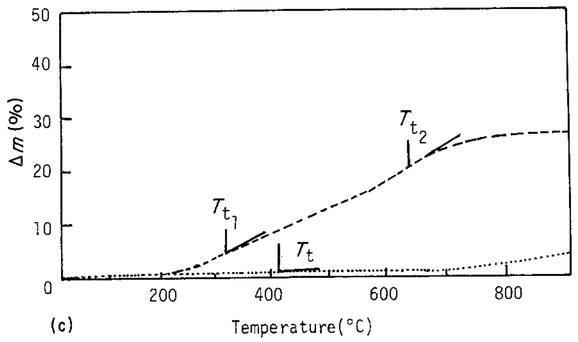


Figure 2 Thermal analysis data. (a) DTA and TG curves of pure nickel metal at a heating rate of 30° C min^{-1}. (b) Schematic DTA curves of pure chromium metal at 10, 30 and 50° C min^{-1}. (c) TG curves of pure copper and chromium metal at a heating rate of 30° C min^{-1}.

powders. The thermal analysis results (Fig. 3) showed that thermogravimetry did not take place for Ni–14.5Cr and Ni–7.67Cu alloy powders.

It is known that some Ni–Cr alloys composed of Ni (69 to 73 wt %) and Cr (11 to 18 wt %) as the main alloy elements, are oxidized more slowly than a high-purity nickel [3]. The kinetics of high-temperature oxidation (800 to 1010° C) of the Ni–Cr alloys agrees with a parabolic rate law. The Arrhenius plot is often used to examine the changes in oxidation mechanism with temperature [1, 3, 12]. At a high temperature of 1000° C, NiO and particularly Cr_2O_3 were predominant in dental nickel-base cast alloys [13]. At 650° C, oxides of nearly all elements contained in the alloys were formed on the alloy surface. The nickel-base alloys contained additive elements such as molybdenum, aluminium and chromium in large amounts [3, 4, 13, 14], because some oxides had the potential to contribute a strong alloy and porcelain bond. NiO and Cr_2O_3 became the predominant oxide species with increasing oxidation temperature in nickel-base dental alloys [13]. At higher temperatures, 985° C, the spinel $NiCr_2O_4$ was formed as a composite film of NiO and Cr_2O_3 in 80Ni–20Cr alloy [15], and Cr_2O_3 oxide film was prompted by chromium-rich microstructure features [16]. The role of individual alloying elements was clarified gradually, and it was clearly observed that a high-content layer of Cr_2O_3 was formed with

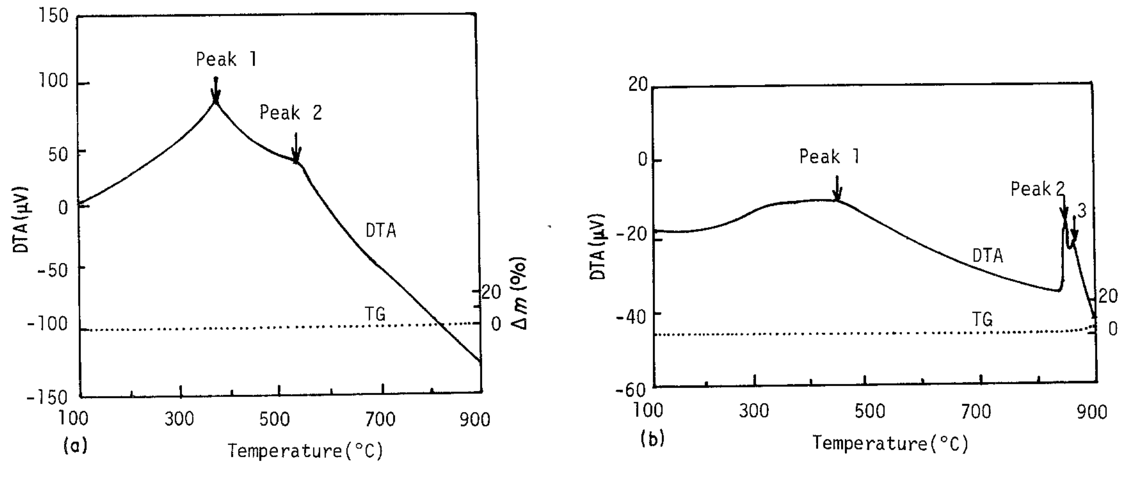


Figure 3 DTA and TG curves: (a) Ni–14.5Cr, (b) Ni–7.67Cu.

TABLE II Transition temperature at heating rates of 10, 30 and 50° C min^{-1} for the metal powders tested

Heating rate (° C min^{-1})	Transition temperature (° C)			
	Ni	Cr	Cu	Cu
10	569.6	398.6	285.6	587.8
30	606.8	420.6	313.6	631.8
50	625.0	432.8	330.2	662.0

increasing oxidation temperature in dental Ni–Cr alloy. In this study, individual alloying elements such as nickel, chromium and copper in nickel-base dental alloys were therefore examined by thermal analysis to clarify the effect of the alloying elements on the thermal behaviour of the nickel-base alloys.

The ternary Ni–Cu–Mn alloys have been examined recently as alternatives to dental Ni–Cr alloys [17, 18], and it is necessary to determine the influence of the alloying elements on the oxide. As a measure of oxidation, the mean transition temperatures at heating rates of 10, 30 and 50° C min^{-1} indicated in Table III increased with increasing heating rates. The alloying elements nickel and chromium had only transition temperatures which were, respectively, equivalent to NiO and Cr_2O_3 oxide formations in the temperature range from room temperature to 900° C, but copper as an alloying element had, respectively, two transition temperatures for CuO and Cu_2O formations [6–9]. As identification of the oxides was difficult at the transition temperatures, the existence of the oxides might be found after cooling to room temperature. It is difficult to identify which ones are found in the X-ray diffraction pattern, because it is known that the oxides are present in mixtures which form oxide layers [6]. Therefore, it is deduced that copper oxides form as complex phases. The oxide layers were formed as complex oxides on high temperature oxidation of gold alloys [12, 19].

The activation energy for the formation of copper oxide at each temperature was calculated. The results show that each activation energy of the copper oxides was 24.2 (low temperature) and 34.5 (higher temperature) kcal mol^{-1}, which were shown in Table II. In the case of oxidation of pure nickel and chromium metals, the values are, respectively, 43.4 (NiO) and 42.3 (Cr_2O_3) kcal mol^{-1}. These values of activation for oxidation agreed fairly well with the data presented previously [6–8, 12]. They indicate that the values ranged from 18.5 to 51.7 kcal mol^{-1}, although their values were affected by such factors as atmosphere, impurity and heating rate.

Thus, it is possible to discuss the activation energy for the oxidation in nickel-base alloys. The values are shown in Table IV. At Peak 1, the value of Ni–14.5Cr alloy was about 45 kcal mol^{-1}. At Peak 2, it had increased after the introduction of chromium and copper alloying elements to the nickel-base alloy. The value at Peak 2 for Ni–14.5Cr alloy was smaller than that for Ni–7.67Cu alloy. The values of activation energy for oxidation in Ni–7.67Cu alloy powders were 69.4, 319.4 and 319.4 kcal mol^{-1}. At Peaks 2 and 3, it was deduced that P_2O_5 was formed because the energy for oxidation was 322.7 kcal mol^{-1} [9]. At higher temperatures, nickel-base alloy powders oxidize more slowly than do pure metals of nickel, chromium and copper. In the nickel-base alloys tested, the formation of SiO_2, B_2O_3 and also Fe_2O_3 should be considered, as reported previously [13]. The results state that these oxides may be found within the other oxide compounds as a complex phase. The identification of these oxides was difficult because they overlapped the other compounds in this study.

TABLE III The change of transition temperature in the metal powders tested at heating rates of 10, 30 and 50° C min^{-1}

Heating rate (° C min^{-1})	Transition temperature (° C)				
	Ni–14.5Cr		Ni–7.67Cu		
10	398.2	622.6	448.0	857.8	873.8
30	417.0	648.3	463.2	860.7	876.3
50	427.5	663.2	471.6	864.8	878.4

TABLE IV Activation energy for the formation of oxides in the metal and alloy powders investigated

Materials	Activation energy (kcal mol^{-1})
Ni	43.4
Cr	42.3
Cu	24.2, 34.5
Ni-14.5Cr	45.0, 68.0
Ni-7.67Cu	69.4, 319.4, 319.4

In summary, it is desirable to know which individual alloying elements have an effect on the oxidation of nickel-base alloys and what values of activation energy in nickel-base alloys are obtained. It is not easy to identify which oxides occur at each temperature of oxide formation in nickel-base alloys containing many alloying elements. The thermal analysis results may, however, clarify that adding copper and chromium to pure nickel metal decreases the production of oxides by a small amount in nickel-base alloys, compared to the pure nickel metal. The activation energy in nickel-base alloys did not have a value smaller than that in pure metals. A future study will examine what amounts of copper and chromium are necessary in nickel-base alloys, and which additive elements should be added to nickel-base alloys to decrease the oxidation of the alloys.

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