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Thermoanalytical study of the oxidation of selected metals with reference to the influence of heating rate

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Abstract

Study of the effect of heating rate on reaction temperature is important in order to understand the kinetic and mechanistic aspects of solid–gas reactions involving metals and alloys. The oxidation behaviour of selected metals has been studied by thermogravimetry as a function of temperature. The dependence of reaction temperature on heating rate has been examined and found to agree well with the generalised Urbanovici–Segal correlation. Nickel and tantalum were taken as typical metallic samples and oxidation of zirconium sponge has also been included in this study in view of our interest in this material.

INTRODUCTION

A knowledge of the kinetic and mechanistic aspects of the oxidation of metals and alloys is essential in understanding the high temperature reactivity of these materials [1]. Influence of heating rate on the rate of a reaction process and on the associated kinetic parameters [2–6] is a matter of relevance in this context. Study of the effect of heating rate on the reaction temperatures forms an essential step in this direction. Urbanovici and Segal proposed a correlation between heating rate and reciprocal of reaction temperature [2]. In the present work, air oxidation of selected metals was studied by thermogravimetry and the observed dependence of reaction temperature on heating rate is explained employing the relationship proposed by Urbanovici and Segal. Nickel and tantalum have been taken as typical metallic samples in the present work. Study of the oxidation of zirconium has also been included as a part of our current interest in the application of zirconium [7] and zirconium based alloys [8].

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EXPERIMENTAL

The sample materials tantalum and zirconium were obtained from Nuclear Fuel Complex, Hyderabad, and nickel was obtained from M/S. Cerac Inc. (purity in all cases 99.9%). While nickel was taken in the form of powder (mesh size, −100) and tantalum in the form of a thin rectangular foil (approximately 6 mm × 4 mm × 0.2 mm), zirconium was taken in the form of a sponge. Oxidation was carried out employing a Netzsch model STA 429 thermal analyser. The experimental runs were taken in the nonisothermal mode following various heating rates in the range 1–20 K min^{-1}. Sample masses were chosen near to 100 mg and recrystallised alumina crucibles were used as sample containers. Oxidation was carried out in flowing air, the flow rate being 75 ml min^{-1}. The mass changes were thermogravimetrically followed covering the temperature range from room temperature to about 1600 K.

RESULTS AND DISCUSSION

From the variation of sample mass as a function of temperature, the fraction reacted (α) was evaluated at various temperatures and is shown in Figs. 1, 2 and 3 for nickel, tantalum and zirconium, respectively. In all the cases a gradual shift in the α versus T curves to the higher temperature regime is noted with increase in heating rate from 1 to 20 K min^{-1}. For selected constant values of α (in the range 0.1–0.9), the observed reaction temperature (T_r) was noted corresponding to the various heating rates. It was seen that the data in all the three cases could be expressed by the

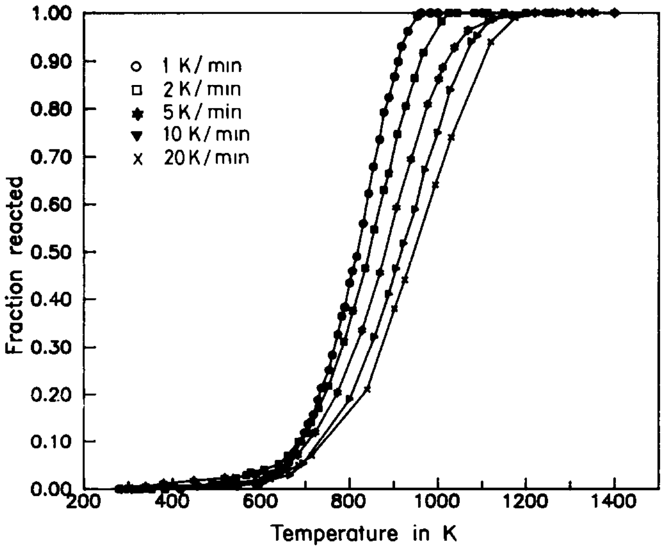

Fig. 1. Fraction reacted (α) as a function of temperature for the oxidation of nickel.

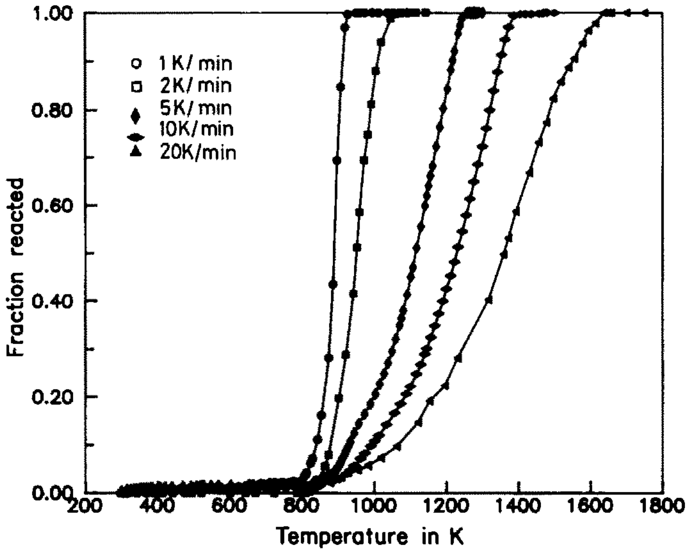

Fig. 2. Fraction reacted (α) as a function of temperature for the oxidation of tantalum.

Urbanovici–Segal relationship [2]

$$1/T_r = A + B \log \beta$$

where T_r is the reaction temperature observed, β is the heating rate and A and B are constants obtained by fitting the curves by the method of least squares.

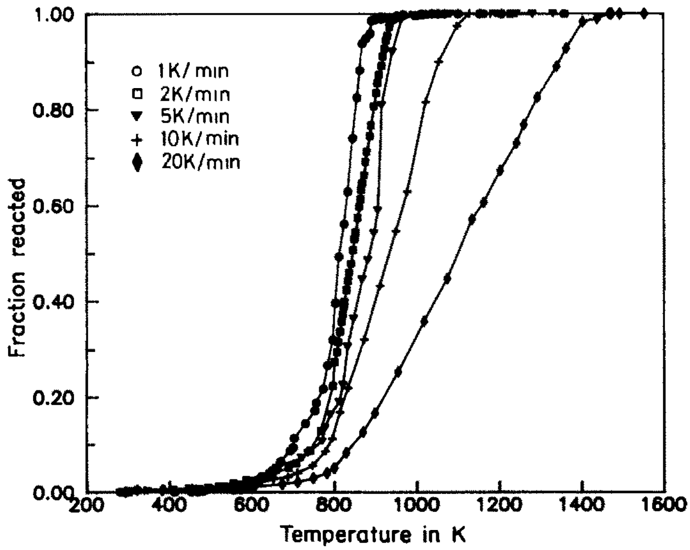

Fig. 3. Fraction reacted (α) as a function of temperature for the oxidation of zirconium.

TABLE 1

Observed and calculated values of reaction temperature at various values of heating rate (β) for the oxidation of nickel

α	A	B	β/K min^{-1}	T_r(obs)/K	T_r(calc)/K	Deviation/%
0.1	1.488817×10^{-3}	-1.05975×10^{-4}	1	676	672	0.59
			2	681	686	0.73
			5	703	704	0.14
			10	732	719	1.78
			20	736	734	0.27
0.2	1.3664×10^{-3}	-1.09663×10^{-4}	1	733	732	0.14
			2	745	750	0.67
			5	776	775	0.13
			10	805	796	1.12
			20	810	817	0.86
0.3	1.30582×10^{-3}	-1.09388×10^{-4}	1	765	766	0.13
			2	786	786	0.00
			5	818	813	0.61
			10	827	836	1.09
			20	864	858	0.69
0.4	1.26348×10^{-3}	-1.30388×10^{-4}	1	794	791	0.38
			2	813	817	0.49
			5	850	853	0.35
			10	890	882	0.90
			20	912	914	0.22
0.6	1.18656×10^{-3}	-1.3141×10^{-4}	1	840	843	0.36
			2	873	872	0.11
			5	916	913	0.33
			10	952	947	0.53
			20	976	985	0.92
0.8	1.13093×10^{-3}	-1.45913×10^{-4}	1	880	884	0.45
			2	923	920	0.33
			5	978	972	0.61
			10	1016	1015	0.10
			20	1057	1062	0.47

Table 1 indicates the constants A and B corresponding to various selected values of α for oxidation of nickel. The observed reaction temperatures at various heating rates together with the temperatures calculated by employing the constants A and B are tabulated. Similar data for oxidation of tantalum and zirconium are presented in Tables 2 and 3 respectively. Figure 4 shows the reciprocal reaction temperatures as a function of log β (corresponding to various values of α) for the oxidation of nickel. Similar plots of reciprocal reaction temperature versus log β for the cases of tantalum and zirconium are shown in Figs. 5 and 6 respectively. It is seen that at a given fractional progress of the reaction, there is a good

TABLE 2

Observed and calculated values of reaction temperature at various values of heating rate (β) for the oxidation of tantalum

α	A	B	β/K min^{-1}	T_r(obs)/ K	T_r(calc)/ K	Deviation/ %
0.1	1.19647×10^{-3}	-1.94078×10^{-4}	1	840	836	0.48
			2	880	879	0.11
			5	930	942	1.29
			10	995	998	0.30
			20	1070	1059	1.03
0.2	1.16782×10^{-3}	-2.44334×10^{-4}	1	862	856	0.70
			2	905	914	0.99
			5	1001	1003	0.20
			10	1090	1083	0.64
			20	1175	1176	0.09
0.3	1.1465×10^{-3}	-2.69211×10^{-4}	1	877	872	0.57
			2	925	938	1.41
			5	1055	1043	1.14
			10	1145	1140	0.44
			20	1248	1256	0.64
0.4	1.13396×10^{-3}	-2.90586×10^{-4}	1	885	882	0.34
			2	945	956	1.16
			5	1085	1074	1.01
			10	1190	1186	0.34
			20	1315	1323	0.61
0.6	1.1172×10^{-3}	-3.19853×10^{-4}	1	898	895	0.33
			2	963	979	1.66
			5	1140	1118	1.93
			10	1268	1254	1.10
			20	1403	1426	1.64
0.8	1.1021×10^{-3}	-3.41968×10^{-4}	1	906	909	0.33
			2	987	1000	1.32
			5	1190	1159	2.61
			10	1330	1316	1.05
			20	1487	1522	2.35

linear correlation between the reciprocal reaction temperature ($1/T_r$) and $\log \beta$ in all the cases. It is also quite interesting to note that the physical form (powder, foil or sponge) of the present metallic samples has not affected the good linear correlations mentioned above. It is felt that heat transport across the oxide/metal interface as well as the bulk of the unreacted metal has a bearing on the magnitude of the slope (B) of the $1/T_r$ versus $\log \beta$ plots, and hence efforts are being made to understand this aspect. Development of any quantitative understanding in this direction is made complex in view of the uncertainties involved in obtaining reliable

TABLE 3

Observed and calculated values of reaction temperature at various values of heating rate (β) for the oxidation of zirconium

α	A	B	β/K min^{-1}	T_r(obs)/K	T_r(calc)/K	Deviation/%
0.1	1.4331×10^{-3}	-1.74952×10^{-4}	1	693	698	0.72
			2	747	724	3.08
			5	739	763	3.25
			10	786	795	1.14
			20	846	830	1.89
0.2	1.3184×10^{-3}	-1.13352×10^{-4}	1	760	762	0.26
			2	786	783	0.38
			5	812	811	0.12
			10	828	834	0.72
			20	862	859	0.34
0.3	1.27719×10^{-3}	-1.4599×10^{-4}	1	791	783	1.01
			2	806	811	0.62
			5	847	851	0.47
			10	897	884	1.45
			20	940	920	2.13
0.4	1.26676×10^{-3}	-2.11695×10^{-4}	1	801	789	1.50
			2	823	831	0.97
			5	865	894	3.35
			10	978	948	3.07
			20	1006	991	1.49
0.6	1.21916×10^{-3}	-2.79542×10^{-4}	1	827	820	0.85
			2	862	881	2.20
			5	994	977	1.71
			10	1068	1064	0.37
			20	1160	1169	0.78
0.8	1.18026×10^{-3}	-3.05447×10^{-4}	1	852	847	0.59
			2	899	919	2.22
			5	1020	1034	1.37
			10	1164	1143	1.80
			20	1253	1277	1.92

thermal diffusivity/thermal conductivity data of porous metal oxides of present interest and modelling diffusivities associated with the description of heat transport along a continuously varying reaction front as the reaction progresses.

CONCLUSIONS

Systematic thermoanalytical studies were carried out on the oxidation behaviour of nickel, tantalum and zirconium with reference to heating rate and it is seen that the variation of the reaction temperature as a function of heating rate follows the Urbanovici–Segal relationship in all the three

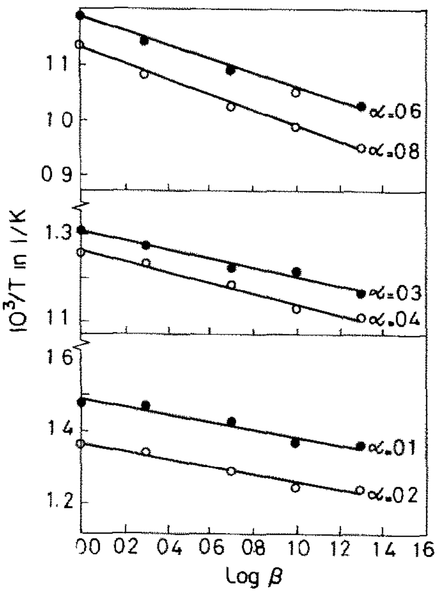

Fig. 4. Variation of the reciprocal of reaction temperature as a function of the logarithm of heating rate for the oxidation of nickel.

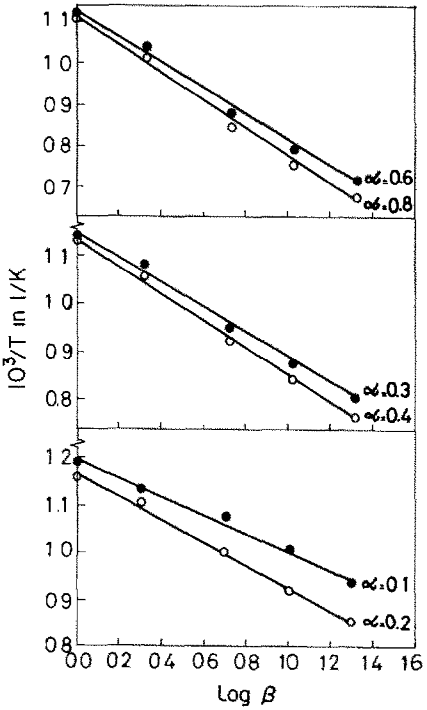

Fig. 5. Variation of the reciprocal of reaction temperature as a function of the logarithm of heating rate for the oxidation of tantalum.

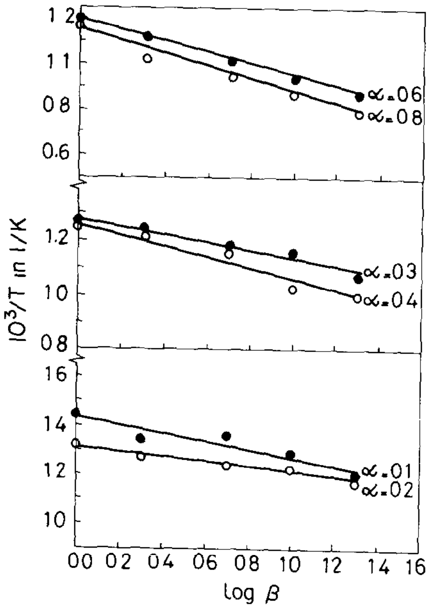

Fig. 6. Variation of the reciprocal of reaction temperature as a function of the logarithm of heating rate for the oxidation of zirconium.

cases. It was also noted that the physical form of the samples has not affected the linear correlation between the heating rate and reciprocal of reaction temperature.

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