Oxidation of Commercial High-Temperature Alloys

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THE kinetics of selective oxidation of chromium in four commercial Ni-(Fe)-Cr superalloys (N 155, DH 242, Hastelloy X, and TD NiCr) were studied. Chemical compositions provided by the manufacturers of these alloys are listed in Table I. All wires were 0.005 ± 0.0005 in. diam. Prior to oxidation testing, the wires were 1) ultrasonically cleaned in hot trichloroethylene followed by an acetone rinse and 2) then annealed at 1150°C (2100°F) for 8 hr in dry hydrogen (below −80°F dewpoint). Wires were loosely wound around prefired mullite tubes for support during the annealing cycle. Small coils weighing about 0.3 to 0.4 g were prepared from 100 in. lengths (nominal) of wire, using finger cots to preserve wire cleanliness.

During air oxidation tests, a coil of wire was suspended from a Cahn Electrobalance having 0.1 µg sensitivity by a platinum wire into an electrically heated tube furnace. Chimney (levitation) effects were substantially eliminated by use of a bell jar closure over the balance and top end of the furnace. The 2-in. diam lower end of the furnace was loosely covered with a porous metal structure (Poroplate^R) to prevent drafts while allowing relatively free access to room air. Two 14 gage chromel-alumel thermocouples measured furnace temperature which was automatically controlled ±10°C by frequently calibrated equipment. Weight gain at a given temperature was recorded continuously for times up to 100 hr. Separate samples were exposed at four or five temperatures in the range 760° to 1149°C (1400° to 2100°F). Further details of the experimental procedure together with the resulting data, which is analyzed herein, have been reported elsewhere.[1]

The oxidation kinetics of the four alloys were all found to obey the parabolic rate law.[2] In many of the tests the oxidation rate exhibited two distinct stages: early and late; while in the others only one stage was observed. The calculated rate constants and time for the early stage of oxidation are given in Table II. In the late stage rate constants varied irregularly. Logarithms of the rate constants for the early stage are plotted as an inverse function of temperature in Fig. 1. TD NiCr is found to be about an order of magnitude more oxidation-resistant than the other alloys. Weight gain at 760°C was particularly small and too uncertain to use here. The other oxidation rates for TD NiCr also exhibited considerable scatter, partly due to very small weight gains; thus the somewhat poorer fit of the data points to the line in Fig. 1(d).

A least-squares fit to the Arrhenius plots in Fig. 1 yields the following equations:

For N 155

$$k = 0.051 \exp[(-60,800 \pm 700)/RT] \quad (g/cm^2)^2/\sec$$

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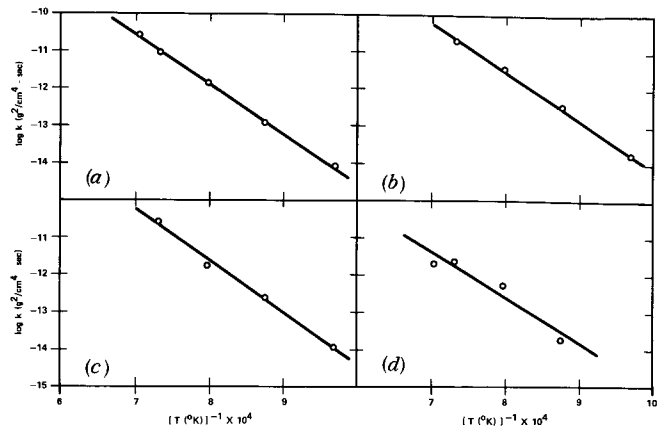
Fig. 1—Temperature dependence of the parabolic rate constants for the oxidation of four different Ni-(Fe)-Cr alloys: (a) N 155, (b) DH 242, (c) Hastelloy X, and (d) TD NiCr.

For DH 242

$$k = 0.075 \exp[(-59,500 \pm 1,000)/RT] \quad (g/cm^2)^2/\sec$$

For Hastelloy X

$$k = 0.24 \exp[(-63,100 \pm 2,300)/RT] \quad (g/cm^2)^2/\sec$$

For TD NiCr

$$k = 0.002 \exp[(-56,400 \pm 9,300)/RT] \quad (g/cm^2)^2/\sec$$

As can be seen, all of the activation energy values are close to the value of 61.1 kcal per mole obtained for chromium ion diffusion in polycrystalline Cr_2O_3 by Hagel and Seybolt,[3] and to the value of 59.4 kcal per mole obtained for oxidation of pure chromium by Gulbransen and Andrew.[4] The results indicate that the rate-controlling mechanism is chromium ion diffusion in the chromium oxide layer, and the activation energy is insensitive to the variation of chemical compositions of the alloys within the experimental accuracy.

X-ray studies of separate strip samples revealed that the oxide scales of TD NiCr and DH 242 consisted of Cr_2O_3 only, and those of Hastelloy X and N 155 were a mixture of Cr_2O_3 and spinel.[5] The spinel phase was found to be embedded as discrete particles in a Cr_2O_3 matrix. Thus, it is probable that chromium ion diffusion in Cr_2O_3 controls the oxidation mechanism. Gulbransen and Andrew[6] as well as Birks and Rickert[7] found Cr_2O_3 to be the main reaction product after extended oxidation of Ni-20 pct Cr and Ni-30 pct Cr alloys at high temperatures. For Ni-Cr alloys containing less than 10 pct Cr, Birks and Rickert[7] proposed that the surface oxide scales consist of two zones of NiO: an outer compact NiO layer, and an inner porous NiO layer with embedded particles of $NiCr_2O_4$, and consequently, nickel ion diffusion in NiO controls the oxidation mechanism. On the other hand, according to Abendroth,[8] the oxide scales formed on Fe-42Ni-5.5Cr-0.36Si-0.26Mn-0.18Al-0.09C (in wt pct) during oxidation in hydrogen-water vapor mixtures consisted primarily of Cr_2O_3, and the activation energy for oxidation was 60.4 kcal per mole, close to the values calculated in this work.

In summary, in all of the four alloys studied, chromium ion diffusion in Cr_2O_3 is rate-controlling for oxidation. When discrete spinel particles are present

Table I. Chemical Compositions of the Alloys, Weight Percent

Alloy	C	Mn	Si	Cr	Ni	Co	Mo	W	Cb + Ta	Fe	Cu	S	P	Other
N 155*	0.06	1.35	0.31	21.07	19.16	19.92	2.72	2.41	1.13	Bal.		0.013	0.018	
DH 242†	0.03	0.08	0.95	19.26	Bal				1.27	0.87	0.02			
Hastelloy X‡	0.09	0.58	0 57	21.57	Bal	1.45	9.08	0.52		18.07		0.004	0.016	
TD NiCr‡	0.011			21.85	Bal							0.006		2.5 ThO$_2$

Wire Source

*National Standard Co
†Driver-Harris Co.
‡Hoskins Manufacturing Co.

Table II. Parabolic Rate Constants for the Early Stage: k, (g/cm^2)^2/sec

	N 155		DH 242		Hastelloy X		TD NiCr	
T°C	k	Time, hr	k	Time, hr	k	Time, hr	k	Time, hr
760	7.59 X 10^{-15}	30	1.75 X 10^{-14}	8	1.12 X 10^{-14}	>100		
871	1.13 X 10^{-13}	8	3.56 X 10^{-13}	4	2.42 X 10^{-13}	>100	1.83 X 10^{-14}	>100
982	1.33 X 10^{-12}	50	3.41 X 10^{-12}	75	1.77 X 10^{-12}	50	5.07 X 10^{-13}	50
1093	9.08 X 10^{-12}	>75	2.04 X 10^{-11}	>100	2.40 X 10^{-11}	50	2.27 X 10^{-12}	4
1149	2.54 X 10^{-11}	16					2.00 X 10^{-12}	8

in the oxide scales, they appear to have little or no effect on the oxidation rate.

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Activity of Copper in Solid Cu-Au Alloys

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DATA has been obtained for the activity of copper in solid Cu-Au alloys as a part of a program to survey the thermodynamic properties of solid Cu-Au-Ag alloys. The measurements were made in an electromotive force cell of the type.

Pt|Cu-Au(alloy) + Cu$_2$O|0.85 ZrO$_2$

$$- 0.15\ CaO|Cu + Cu_2O|Pt$$
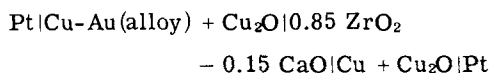
The general configuration of the equipment was patterned after Rapp and Maak.[1] A modification that resulted in improved stability of the measured electromotive forces was the use of the electrolyte in the form of cylindrical crucible ($\frac{1}{2}$ in. diam by 1 in. length). The reference pellet (Cu + Cu$_2$O) was pressed against the outside and the alloy pellet against the inside of the crucible base. This procedure reduces the migration of metal through the gas phase and along the electrolyte surface by greatly increasing the diffusion path and hence reduces the drift in measured electromotive forces.

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Table I. Activity Data in the Cu-Au System

Pct Cu	Temp, °C	EMF, mv	dE/dt, 825°C, μV/°C	a_{Cu}	γ_{Cu}
20	825	256		0.066	0.33
60	825	84 36	46.7	0.409	0.682
	825	83 85		0.411	0.685
	875	86.42		0.417	0.696
80	829	27.85	22.7	0.746	0.932
	829	27.25		0.750	0.938
	723	25.45		0.745	0.932
	877	28.78		0.748	0.935
85	824	17.60	15 8	0.830	0.976
	722	16.15		0.828	0.974
	817	17.30		0.832	0.980
	879	18.55		0.829	0.975
90	825	10.75	11.6	0.892	0.991
	721	9 50		0.895	0.995
	874	11.30		0.892	0.991
95	824	4.90	4.6	0.9495	1.000
	724	4.60		0.940	0.998
	877	5.15		0.9495	1.000
	916	5.47		0.948	0.998
98	826	1.70	1.35	0.982	1.002
	900	2.70		0.974	0.994