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THE EFFECT OF Cr, Co, Al, Mo, and Ta ON THE CYCLIC OXIDATION BEHAVIOR OF A PROTOTYPE CAST Ni-BASE SUPERALLOY BASED ON A 2^5 COMPOSITE STATISTICALLY DESIGNED EXPERIMENT

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SUMMARY

A series of cast Ni-base γ/γ' superalloys with nominally fixed levels of 1 wt % Ti, 2 wt % W, 1 wt % Cb, 0.10 wt % Zr, 0.12 wt % C and 0.01 wt % B were systematically varied at selected levels of Co, Cr, Mo, Ta, and Al. The alloy compositions were based on a full 2^5 factorial statistical design supplemented by 10 star point alloys and a center point alloy. This full central composite design of 43 alloys allows a complete second degree (main effect, 2 factor interaction and square terms) estimating equation to be derived from the 5-compositional variables. The elemental levels varied were Mo, 0 to 4 percent; Cr, 6 to 18 percent; Co, 0 to 20 percent, Ta, 0 to 8 percent; and Al, 3.25 to 6.25 percent. The cyclic oxidation resistance was determined from specific weight change data as a function of time for 1 hr cycles in static air at 1100° C. A derived oxidation attack parameter, log Ka, was fitted over the alloy sample space. At a rejection level of 0.90, eleven of the 25 (including five for the variability of Ti, W, Cr, Zr and C) coefficients were significant and explained 93 percent of the total variability. The significant terms in decreasing order of their importance were Al, Ta, Cr, Cr^2, Al•Cr, Cr•Co, Co^2, Al•Mo, Cr•Mo, Al•Al and Mo•Ta. The Al term alone accounted for close to 82 percent of the explained variability. The estimating equation showed that the Al level was the most important and should be at its 6.25 wt % maximum value. The Mo and Ta levels should also be at their maximum 4 and 8 wt % respectively. The cobalt composition should be as low as possible, i.e., 0 wt %. The Cr level optimum will vary depending on the other 4 levels. Here minimum oxidation occurs at 7.0 wt % Cr. If the alloy were fixed at 10 wt % Co, as in most commercial alloys, the Cr optimum shifts to 9.5 wt %. The X-ray diffraction results indicate the most protective scales are alumina/aluminate spinel stabilized with a tri-rutile oxide high in Ta and Mo.

INTRODUCTION

An earlier series studies (refs. 1 and 2) detailed the effect of two non-zero levels of Cr, Al, Ti, Mo, W, Ta and Cb on various properties of a typical Ni-base γ/γ' superalloy cast turbine alloy. The properties included structure, cyclic oxidation resistance, stress rupture and hot corrosion resistance.

Based on these results and on the possible shortage of critical alloy elements like Cr (ref. 3) a comparable program was initiated to study a similar Ni-base γ/γ' type turbine alloy varying five critical alloy additions - Cr, Co, Al, Mo and Ta that were chosen for study. The strategy was not only to test two-levels completely (e.g., a full factorial) as compared to a 1/4 by 2^7 fractional factorial used in the previous program but also to add a center point alloy composition and five sets of star points to completely map the particular response (e.g., stress rupture life). This is termed a central composite design. This is analogous to figure 1 which shows the same approach for just two variables such as Cr and Al. Thus, five levels for each alloy constituent is represented by $2^2 + 2 \times 2 + 1$ and thus involves nine alloy compositions. For five elemental variables 43 alloy compositions are required based on the $5^2 + 5 \times 2 + 1$ giving five levels for each elemental variable. By regression analysis a complete second degree estimating equation can be derived for any given response variable (ref. 4).

PROCEDURE

The basic levels of the five compositional variables are schematically designated as 0, 1, 2, 3, and 4 where the 2 values are the center point of the design. Table I shows the actual weight percent (wt %) corresponding to the five levels. The basic composition of the prototype alloy was chosen as Ni - 1 wt %, Ti - 2 wt %, W - 1 wt %, Cb - 0.10 wt %, Zr - 0.01 wt %, B - 0.12 wt % C. The five range of levels chosen for the five alloying elements represent their range in commercial alloys. Thus, the center point alloy designated as (22222) would be the basic composition with part of the Ni replaced by - 4.75 Al - 12 Cr - 10 Co - 2 Mo - 4 Ta. By a similar designation the alloy coded, for example, as (00113) has the basic composition with 3.25 Al - 6 Cr - 5 Co - 1 Mo - 6 Ta.

The master heats of the 43 alloys were prepared by vacuum induction melting by Howmet Turbine Components Corporation of Dover, New Jersey as 3 in diameter ingots each weighing approximately 40 lb. The master heat ingots were then used to make up individual investment frame castings vacuum induction melted and cast by Duradyne Technologies, Inc. of Mentor, Ohio. Included on each frame were 12 round coating bars; 12 tensile/stress rupture bars, 12 round burner rig bars and 16 rectangular oxidation leaves.

Table II lists the compositions for each alloy. In all cases, the target and actual chemistries were extremely close, to within 10 percent of the target chemistries. The individual oxidation sample coupons were checked by X-ray fluorescence using commercial alloy standards. Each oxidation leaf, nominally 2.54 by 5.0 by 0.254 cm; was machined into four oxidation test coupons each 1 by 2 by 0.23 cm with a 0.3 cm diameter hanger hole. The samples, after cleaning and weighing, were automatically cycled in static air furnaces as described in reference 5. In this study, the samples were tested for 1 hr cycles consisting of 1 hr at 1100° C in the furnace and a minimum of 20 min above the furnace at a temperature of near 65° C. The samples were removed for weighing at 1, 15, 30, 45, 60, 75, 90, 100, 115, 130, 145, 180, 175, 190, and 200 hr to generate a specific weight change versus time curve.

In addition to the weight change data, each sample and its collected spall, was removed and analyzed by X-ray diffraction after 1, 100, and 200 hr.

RESULTS AND DISCUSSION

At 1100° C a total of 53 samples were tested including eight replicates at the center point of the design alloy designated as (22222) and duplicates of

(31131), (33133), (22242), and (24222). All the alloys were run for 200 1 hr cycles except (11111), (11311), (11131), (11331), and (11333) which had to be terminated near the 100 cycle time due to massive sample weight loss and spalling.

Initially, the entire test interval of specific weight change/time data was fitted to the paralinear model equation:

$$\Delta W/A = K_1^{1/2} t^{1/2} - k_2 t \pm \text{SEE} \tag{1}$$

with a rejection level of 0.90.

This lead to an attack parameter defined as:

$$\text{Ka} = (k_1^{1/2} + 10.k_2) \tag{2}$$

In certain cases a more appropriate estimating equation is a simple linear fit:

$$\Delta WA = -k_2 t \pm \text{SEE} \tag{3}$$

which modifies the attach parameters to:

$$\text{Ka} = (20.k_2) \tag{4}$$

These equations and their rationale have been discussed previously references 1 and 5. It was shown that equations (2) and (4) are nearly equivalent and can be related directly to a measured thickness change of the test samples. The 53 individual data sets were fitted first to equation (1) by a multiple linear regression program (ref. 6) but used data only out to 100 hr. If the significance level of either $k_1^{1/2}$ or k_2 did not exceed 0.90, it was dropped and the regression equation recalculated. If both coefficients were less than 0.90, the one with the lower probability was dropped first. Table III lists the derived coefficients for each test sample. If the $k_1^{1/2}$ column contains a 0.0 value, only the k_2 linear term was considered significant and thus followed equation (3). Of the 53 tests, 26 followed equation (3). Of these, 12 runs, marked with a superscript 1 gave a $-k^{1/2}$ coefficient only when fitted initially to equation (1). These were forced to the linear form rather than use a $-k_1^{1/2}$ value.

These values were next converted to their appropriate Ka value using either equations (2) or (4). These Ka values are listed in the next column. Listed in the adjacent column is the specific sample weight loss after 100 hr. The Ka values and the weight loss are highly associated with a correlation coefficient of 0.971. Some specific weight change versus time plots are shown in figures 2 to 5 indicating some of the extremes of the data, the types of curves and their fits to equations (1) or (3). Figure 2 shows the plots for three of the eight center point (22222) alloy samples. All eight were fitted to equation (3). A comparison of all eight of the curves showed that they were quite similar out to 100 hr then tended to diverge as shown in the figure. This tendency for "breakaway" similar to going from second to third stage creep in stress rupture testing led to fitting equations (3) or (1) where used to just the first 100 of the 200 hr data points. This divergence after 100 hr was present in the other replicates as well. In the five tests mentioned earlier which could only be tested to about 100 hr, only five or six points rather than eight (i.e., 200 hr) were used to fit the data. Figure 3 shows two of the 12 sets of data where an initial $-k_1^{1/2}$ coefficient led to forcing a $-k_2$ curve fit. These data plots tend to be concave up with time and were difficult to explain mechanistically. This effect may be due to $k_1^{1/2}$ and/or k_2 varying with time. Figure 4 shows two of the remaining pure linear curve fits that followed naturally from the curve fitting procedure. This results when spalling is considerably more significant than scale growth. Finally, figure 5 shows data curve fits where scale growth, $k_1^{1/2}$ and scale spalling, k_2 are both significant and follow a classic paralinear model.

The next step is to run a multiple regression analysis of Ka as a function of the compositional variables. Because of the nature of the balanced design of the experiment, the following second degree model estimating equation can be used where the elemental symbols stand for weight percent of each alloy constituent:

$$\begin{aligned}Y = {} & A_0 + b_1\mathrm{Al} + b_2\mathrm{Cr} + b_3\mathrm{Co} + b_4\mathrm{Mo} + b_5\mathrm{Ta} \\ & + b_6\mathrm{Al}^2 + b_7\mathrm{Cr}^2 + b_8\mathrm{Co}^2 + b_9\mathrm{Mo}^2 + b_{10}\mathrm{Ta}^2 \\ & + b_{11}\mathrm{Al}\cdot\mathrm{Cr} + b_{12}\mathrm{Al}\cdot\mathrm{Co} + b_{13}\mathrm{Al}\cdot\mathrm{Mo} + b_{14}\mathrm{Al}\cdot\mathrm{Ta} \\ & + b_{15}\mathrm{Cr}\cdot\mathrm{Co} + b_{16}\mathrm{Cr}\cdot\mathrm{Mo} + b_{17}\mathrm{Cr}\cdot\mathrm{Ta} + b \\ & + b_{18}\mathrm{Co}\cdot\mathrm{Mo} + b_{19}\mathrm{Co}\cdot\mathrm{Ta} + b_{20}\mathrm{Mo}\cdot\mathrm{Ta} \pm \mathrm{SEE}\end{aligned} \tag{5}$$

In addition to the following tramp variables were added extending equation (5) to:

$$+ b_{21}\mathrm{Ti} + b_{22}\mathrm{Cb} + b_{23}\mathrm{W} + b_{24}\mathrm{Zr} + b_{25}\mathrm{C}$$

Equation (5) was analyzed and the data manipulated by means of <u>MINITAB</u>, release 81.1 on an IBM 370 main frame computer. In addition all of the compositional variables were first "centered" by subtracting the mean of the weight percent of each compositional variable from each individual compositional value for each sample. This tends to minimize the correlation between the linear and higher order terms sometimes leading to bias in estimating the coefficients (ref. 7).

While use of the independent variables particularly in a statistically designed experiment is fairly straightforward, the choice of what transformation to use on Ka is not so clear cut. A simple linear fit with Y = Ka with a rejection level of 0.90 reduces to an estimating equation of 11 terms from the original 25, but has the disadvantage that 15 of the 53 estimates are negative. Using $\log_{10}$ Ka = Y as was used in reference 1 was the next obvious choice and eliminates the minus values for Ka estimates, but also could give quite large estimates for samples slightly outside the alloy content space. It also reduces to 11 significant coefficients with a nearly identical value of R^2 of 93 percent compared to that of the linear case of R^2 = 94 percent.

Table IV shows the original derived Ka along with Ka estimates for each of the two regression cases. For the log Ka the antilogs are listed for direct comparison. Not only does the $\log_{10}$ Ka transformation eliminate negative Ka estimates, it actually gives better Ka estimates in the lower value regime (i.e., Ka values of close to 2 or less) than the linear estimate. Of 17 such values in table IV the $\log_{10}$ Ka fit transformed to direct Ka estimates were much closer than the linear estimates in all 17 cases. Since estimation in the low Ka range was considered more critical, the $\log_{10}$ Ka transform was chosen to make the detailed analysis of the data.

Table V shows a summary of the regression analysis in terms of the $\log_{10}$ transform of Ka. It can be seen that the Al effect is by far the most important accounting for almost 82 percent of the total explained variability and with its three interaction terms close to 85 percent. Of most interest are the negative coefficients that lower the Ka estimates thus minimizing the rate of cyclic oxidation. The 11 coefficients make interpretation difficult but the Al effect is so strong that it overrides the other four alloy additions and is set at its highest level, 6.25 wt % which then locate the other levels to determine the minimum Ka estimate. One way to determine the Ka estimates is to solve the estimating equation over the sample space range of compositions and scan the results for the overall minimum or for any minimum at for example a 10 wt % level which is typical for most commercial Ni-base γ/γ' alloys. A special computer program was written to perform these calculations and scan the results. A minimum is predicted for this alloy at 0 wt % Co - 8. wt % Ta - 4. wt % - 6.25 wt % and close to 7, wt % Cr. If the Co level is fixed at 10.wt % Co only the Cr value changes to near 9.5 wt %.

In general the log Ka data fits quite well as shown in figure 6 with only one possible outlier alloy, 31331, where the observed value is much higher. In addition the replication error is quite small. It is much less than 1 percent of the total variability even though it accounts for eight of the 52 degrees of freedom. This tends to reconfirm the validity of the single Ka parameter approach for analyzing cyclic oxidation data. Its major weakness is that it is difficult to use it to embody complex oxidation/spalling behavior (ref. 8).

In general the large body of X-ray data can be summarized as falling into two general categories. One group with Al levels of 2 (4.75 wt %) and higher tended to form mostly Al_2O_3, 8.10 A aluminate spinel, and with longer times NiO. Any spall was mostly NiO. Tri-rutile type oxides were present at all times. This type of scale formation was associated with the lowest Ka values giving the best oxidation resistance.

The second group was associated more with higher Cr levels of 3 (12.0 wt %) or higher with Al values of less than level 2. Here with lower times mostly NiO, 8.25 A chromite spinel and some Cr_2O_3 were detected. Again, tri-rutile oxides were observed. Occasionally with both types of oxides MoO_2 or Ni (W, Mo) O_4 was detected but apparently did not increase the oxidation rate. Again, as in reference 1 the tri-rutile type oxide when present with alumina/aluminate spinel formers seemed to increase oxidation resistance. In this case Mo and Ta both appear to benefit the oxidation resistance by forming tapolite, the tri-rutile type oxide that appeared to stabilize aluminate formation (ref. 9). On the other hand, low levels of both Al and Cr led directly to NiO formation with high oxide growth rates and massive spalling. The alloy in the sample space with the best oxidation resistance should be very strong alumina/aluminate spinel former.

The regression analysis of the weight change data and subsequent X-ray data indicate the importance of Al and the necessity to balance its content with the Cr composition. Table VI shows the Cr value required at each Al level to give minimum oxidation attack (i.e., lowest $\log_{10}$ Ka value) at three typical cobalt levels - 0, 5, and 10 wt %. These were computed at the maximum Mo and Ta levels. The implication of Cr optimums is that at least at the higher Al levels the alloy is basically an alumina/aluminate spinel former with good cyclic oxidation resistance. At the higher of the $\log_{10}$ Ka minimums the alloy tends to form the less protective chromia/chromite spinel. It should be pointed out that table VI shows the sizeable difference in oxidation resistance since the antilogs (Ka's) vary by a factor of well over 1000. They range from alloys with massive oxidation and spalling to alloys with extremely good oxidation resistance.

SUMMARY AND RESULTS

A series of case Ni-base γ/γ' superalloys with nominally fixed levels of 1 wt % T, 2 wt % W, 1 wt % Cb. 0.10 wt % Zr, 0.12 wt % C and 0.01 wt % B were systematically varied at selected levels of Co, Cr, Mo, Ta, and Al. The alloy compositions studied were based on a statistically designed experiment termed a central composite designed based on 43 compositions. The results were generalized over a sample content space in weight percent of Al 3.25 to 6.25, Cr 6 to 18, Co 0 to 20, Mo 0 to 4, and Ta 0 to 8.

The cyclic oxidation resistance was the response to be studied. This series of alloys was characterized by an oxidation attack parameter, Ka derived from the sample specific weight change based on 1100° C one hour cyclic tests time data. X-ray diffraction analysis of the surface and spall at times was used to supplement the gravimetric results. The $\log_{10}$ Ka transform of this parameter was used as the dependent variable in a multiple linear regression analysis of 20 main, 2 factor interaction and square term-effects of the 5 compositional variables as well as the five main effect variables, Ti, W, Cb, Zr and C around their ±10 percent random variability. Using centered data and a rejection level of 0.90 a $\log_{10}$ Ka estimating equation was derived based on 53 test values that explained 93 percent of the total variability reduced to 11 coefficients.

The results indicated that the Al main effect is by far the most important accounting for close to 82 percent of the regression, and should be as close to the 6.25 wt % maximum as possible. The Co level should be as low as possible while Mo and Ta should be at their maximums at 4 and 8 wt %. The optimum Cr level depends on the other levels. At the maximum Al, Mo and Ta levels, the optimum Cr levels are 7.0, 8.0, and 9.5 wt %, respectively at 0, 5, and 10 wt % Co.

The X-ray diffraction results indicate the best oxidation resistance is associated with alumina/aluminate spinel formation stabilized by a tri-rutile type oxide high in refractory metal, here Mo and Ta.

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TABLE I. - ALLOY CODE LEVELS CONVERTED TO TARGET CHEMISTRIES FOR PROTOTYPE NICKEL ON BASE TEST ALLOY Ni-2.0 wt %, W-1.0 wt %, Cb-1.0 wt %, Ti-0.10 wt %, Zr-0.12 wt %, C-0.01 wt %, B

Alloy element	Alloy code, wt %				
	0	1	2	3	4
Al	3.25	4	4.75	5.50	6.25
Cr	6	9	12	15	18
Co	0	5	10	15	20
Mo	0	1	2	3	4
Ta	0	2	4	6	8

TABLE II. - INGOT CHEMISTRY FOR PROTOTYPE Ni-BASE TEST ALLOY(S)
WITH VARYING Al, Cr, Co, Mo and Ta LEVELS

	ALLOY									
No.	Al	Cr	Co	Mo	Ta	Al	Cr	Co	Mo	Ta
1	1	1	1	1	1	3.86	8.99	4.94	.98	1.99
2	1	1	3	1	1	3.95	8.95	14.83	1.01	1.99
3	1	3	1	1	1	4.20	15.41	4.82	.97	2.14
4	1	3	3	1	1	3.87	13.73	14.67	.98	2.11
5	3	1	1	1	1	5.30	9.07	4.99	.99	2.01
6	3	1	3	1	1	5.43	9.05	15.12	1.01	1.98
7	3	3	1	1	1	5.47	15.10	5.09	1.02	2.02
8	3	3	3	1	1	5.43	15.14	15.25	1.02	2.01
9	1	1	1	1	3	3.92	9.05	4.98	.94	5.94
10	1	1	3	1	3	4.06	8.97	15.21	1.07	6.00
11	1	3	1	1	3	4.01	15.06	4.93	1.10	5.98
12	1	3	3	1	3	4.03	14.70	14.66	1.05	5.82
13	3	1	1	1	3	5.46	9.09	4.98	.97	6.01
14	3	1	3	1	3	5.74	8.27	15.84	.97	6.30
15	3	3	1	1	3	5.70	15.07	4.57	1.06	6.15
16	3	3	3	1	3	5.49	15.20	15.10	.99	6.02
17	1	1	1	3	1	3.97	9.00	5.04	2.97	2.02
18	1	1	3	3	1	3.98	8.93	14.95	2.97	1.92
19	1	3	1	3	1	3.98	14.96	5.02	3.03	2.03
20	1	3	3	3	1	4.05	14.91	14.88	3.08	1.96
21	3	1	1	3	1	5.44	9.08	5.10	3.00	2.02
22	3	1	3	3	1	5.45	9.00	14.95	3.02	2.00
23	3	3	1	3	1	5.47	15.05	5.03	3.03	2.05
24	3	3	3	3	1	5.58	15.09	15.08	3.08	1.97
25	1	1	1	3	3	3.98	8.93	4.92	2.86	5.98
26	1	1	3	3	3	4.05	8.70	15.34	2.83	5.74
27	1	3	1	3	3	4.11	14.84	4.93	2.92	5.99
28	1	3	3	3	3	4.11	15.09	14.80	2.96	6.01
29	3	1	1	3	3	5.51	8.90	4.85	2.87	5.90
30	3	1	3	3	3	5.47	9.02	15.01	2.92	6.07
31	3	3	1	3	3	5.50	15.00	5.05	2.98	6.01
32	3	3	3	3	3	5.55	15.02	15.00	2.96	6.06
33	2	2	2	2	2	5.01	12.94	10.68	2.14	4.26
34	2	2	2	0	2	4.77	11.53	10.36	0.0	4.25
35	2	2	2	4	2	4.81	11.98	10.00	3.97	3.83
36	2	0	2	2	2	4.80(1)	6.11	9.99	1.94	4.11
37	2	4	2	2	2	4.85	18.24	10.26	2.00	4.01
38	2	2	0	2	2	4.91	11.22	0.0	1.93	4.23
39	2	2	4	2	2	4.88	11.91	20.11	2.01	4.00
40	2	2	2	2	0	4.59	12.70	9.00	1.94	0.0
41	2	2	2	2	4	4.85	11.87	9.91	1.92	7.94
42	0	2	2	2	2	3.54	12.37	10.26	2.20	4.22
43	4	2	2	2	2	6.17	12.13	10.10	2.06	3.74

(1) Lost in remelting for test samples.

Fixed Elements:

Ti range .92 to 1.09 w/o
W range 1.88 to 2.16 w/o
Cb range .90 to 1.06 w/o
Zr range .05 to .11 w/o
C range .08 to .12 w/o
B all .01 w/o

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TABLE III. - TEST PARAMETERS FOR PROTOTYPE ALLOYS FROM SPECIFIC WEIGHT CHANGE/TIME DATA FOR ONE HOUR CYCLIC TESTS FOR 200 hr AT 1100° C IN STATIC AIR

Run			ALLOY			1/2			-ΔW/A C
No.	Al	Cr	Co	Mo	Ta	K1	-K2	Ka	100 Hrs.
1	1	1	1	1	1	29.4725	8.440625	113.87870	495.55
2	1	1	3	1	1	0.0	4.392439	87.84878	577.80
3	1	3	1	1	1	10.5992	1.818892	28.78809	89.77
4	1	3	3	1	1	17.48445	3.404206	51.52651	171.64
5	3	1	1	1	1	3.06832	.626754	9.33586	34.32
6	3	1	3	1	1	4.33154	.880539	13.13693	46.56
7	3	3	1	1	1	0.0	.100386	2.00772	9.32
8	3	3	3	1	1	.393811	.096646	1.36027	5.21
9	1	1	1	1	3	30.09413	5.567846	85.77259	266.55
10	1	1	3	1	3	16.20565	4.796237	64.16812	302.59
11	1	3	1	1	3	3.04230	.523490	8.27720	23.55
12	1	3	3	1	3	1.37965	.376776	5.14741	23.00
13	3	1	1	1	3	.188148	.034136	.52951	1.47
14	3	1	3	1	3	.240638	.038454	.62518	1.45
15	3	3	1	1	3	0.0	.020483 (1)	.40966	2.17
16	3	3	3	1	3	0.0	.014994	.29988	1.41
17	1	1	1	3	1	36.43759	8.87290	125.16561	497.74 (2)
18	1	1	3	3	1	36.85310	12.137411	158.22721	748.48
19	1	3	1	3	1	6.91312	1.232810	19.24122	57.24
20	1	3	3	3	1	18.99266	3.388049	52.87315	156.98
21	3	1	1	3	1	0.0	.040537	.81074	3.87
22	3	1	1	3	1	0.0	.051260	1.02520	4.53
23	3	1	3	3	1	3.85190	.910333 (1)	12.95523	60.70
24	3	3	1	3	1	0.0	.118181 (1)	2.36362	9.63
25	3	3	3	3	1	0.0	.037022	.74044	3.02
26	1	1	1	3	3	28.42180	5.379007	82.21187	261.54
27	1	1	3	3	3	27.51647	7.439241	101.90888	486.45
28	1	3	1	3	3	8.34937	1.323829	21.58766	66.43
29	1	3	3	3	3	10.53404	1.754831	28.08235	82.03
30	3	1	1	3	3	.22838	.047494	.70332	2.30
31	3	1	3	3	3	0.0	.015924 (1)	.31848	1.73
32	3	3	1	3	3	0.0	.039422 (1)	.78844	3.30
33	3	3	1	3	3	0.0	.038019 (1)	.76038	3.29
34	3	3	3	3	3	0.0	.036350	.72700	2.89
35	2	2	2	2	2	0.0	.140024	2.80048	12.53
36	2	2	2	2	2	0.0	.134840	2.69684	11.44
37	2	2	2	2	2	0.0	.142955	2.85910	12.52
38	2	2	2	2	2	0.0	.13560 (1)	2.71200	11.46
39	2	2	2	2	2	0.0	.134133 (1)	2.68266	11.15
40	2	2	2	2	2	0.0	.168340	3.36680	14.94
41	2	2	2	2	2	0.0	.143293	2.86586	13.19
42	2	2	2	2	2	0.0	.118800	2.37600	11.01
43	2	2	2	0	2	2.227269	.498384	7.21611	28.84
44	2	2	2	4	2	0.0	.152044 (1)	3.04088	14.30
45	2	2	2	4	2	0.0 (3)	.132446	2.64892	11.75
46	2	0	2	2	2	---	---	---	---
47	2	4	2	2	2	1.261145	.276591	4.02706	13.36
48	2	4	2	2	2	1.422500	.263112	4.05362	11.17

TABLE III. - CONCLUDED.

Run			ALLOY			1/2			-ΔW/A C
No.	Al	Cr	Co	Mo	Ta	K1	-K2	Ka	100 Hrs.
49	2	2	0	2	2	.443537	.025484	.69838	1.63
50	2	2	4	2	2	0.0	.101331 (1)	2.02660	8.14
51	2	2	2	2	0	10.142736	3.795252	48.09526	271.54
52	2	2	2	2	4	0.0	0.058686 (1)	1.17372	4.96
53	0	2	2	2	2	22.28963	4.548979	67.77942	231.14
54	4	2	2	2	2	.091737	.0279045	.36219	1.81

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(1) Data forced to $\Delta W/A = -K2t$ model due to $-K_1^{1/2}$ value in initial data fit.

(2) Extrapolated from 90 to 100 hours.

(3) Not available, lost on remelt.

TABLE IV. - Ka VALUES, EXPERIMENTAL AND DERIVED FROM MULTIPLE REGRESSION ANALYSIS AS FUNCTION OF ALLOY COMPOSITION USING TWO TRANSFORMATIONS OF Ka

Run No.	ALLOY					Ka Observed	Ka - REGRESSION ESTIMATES[1]	
	Al	Cr	Co	Mo	Ta		Y = Ka	Y=Log10Ka
1	1	1	1	1	1	113.879	118.970	153.964
2	1	1	3	1	1	87.849	103.493	217.994
3	1	3	1	1	1	28.788	22.429	17.773
4	1	3	3	1	1	51.527	42.288	29.102
5	3	1	1	1	1	9.336	18.340	7.295
6	3	1	3	1	1	13.137	5.257	9.130
7	3	3	1	1	1	2.007	9.386	3.109
8	3	3	3	1	1	1.360	1.197	2.038
9	1	1	1	1	3	85.773	83.946	46.068
10	1	1	3	1	3	64.168	67.463	54.523
11	1	3	1	1	3	8.277	6.841	8.829
12	1	3	3	1	3	5.147	1.662	6.347
13	3	1	1	1	3	.530	7.249	.741
14	3	1	3	1	3	.625	-2.051	.659
15	3	3	1	1	3	.410	12.156	.256
16	3	3	3	1	3	.300	-2.125	.267
17	1	1	1	3	1	125.165	118.943	83.192
18	1	1	3	3	1	158.227	125.549	138.348
19	1	3	1	3	1	19.241	45.599	41.201
20	1	3	3	3	1	52.873	50.067	24.319
21	3	1	1	3	1	.811	3.262	1.596
22	3	1	1	3	1	1.025	"	"
23	3	1	3	3	1	12.955	9.944	2.541
24	3	3	1	3	1	2.364	-.734	2.040
25	3	3	3	3	1	.740	6.705	1.058
26	1	1	1	3	3	82.212	91.459	60.315
27	1	1	3	3	3	101.909	95.463	90.303
28	1	3	1	3	3	21.588	13.554	21.178
29	1	3	3	3	3	28.082	18.430	14.633
30	3	1	1	3	3	.703	-3.028	.442
31	3	1	3	3	3	.318	4.072	.783
32	3	3	1	3	3	.788	-4.816	.614
33	3	3	1	3	3	.760	"	"
34	3	3	3	3	3	.727	2.596	.345
35	2	2	2	2	2	2.800	-1.566	2.958
36	2	2	2	2	2	2.697	"	"
37	2	2	2	2	2	2.859	"	"
38	2	2	2	2	2	2.712	"	"
39	2	2	2	2	2	2.683	"	"
40	2	2	2	2	2	3.367	"	"
41	2	2	2	2	2	2.866	"	"
42	2	2	2	2	2	2.376	"	"
43	2	2	2	0	2	7.216	4.418	6.715
44	2	2	2	4	2	3.041	15.873	5.634
45	2	2	2	4	2	2.649	"	"
46	2	0	2	2	2	--- (3)	---	---

TABLE IV. - CONCLUDED.

	ALLOY						Ka - REGRESSION ESTIMATES[1]	
Run No.	Al	Cr	Co	Mo	Ta	Ka Observed	Y = Ka	Y=Log10Ka
47	2	4	2	2	2	4.027	5.445	5.596
48	2	4	2	2	2	4.054	"	"
49	2	2	0	2	2	.698	9.634	1.614
50	2	2	4	2	2	2.027	5.996	1.971
51	2	2	2	2	0	48.095	44.462	24.531
52	2	2	2	2	4	1.174	7.143	1.637
53	0	2	2	2	2	67.779	79.896	107.813
54	4	2	2	2	2	.362	-7.596	.263

TABLE V. - COEFFICIENTS OF THE REGRESSION EQUATION FOR $\log_{10}$ Ka AS A FUNCTION OF ALLOY COMPOSITION IN WEIGHT PERCENT FOR 2^5 COMPOSITE DESIGN FOR CENTERED VALUES OF Al, Cr, Co, Mo, AND Ta ALONG WITH LINEAR EFFECTS OF FIVE FIXED ALLOY ELEMENTS - Ti, W, Cb, Zr, AND C (B - NO VARIATION)

	Final Z	Coefficient	t-ratio statistic	Percent of explained SSQS
1	Al	-1.01619	-19.71	81.59
2	Ta	-0.12308	-6.50	7.56
3	Cr	-.05950	-4.73	3.21
4	Cr^2	- .012234	2.62	1.28
5	Al·Cr	.04853	2.62	1.18
6	Cr·Co	-.006711	-2.50	1.18
7	Co^2	-.004167	-2.44	1.03
8	Cr·Mo	.03055	2.1[illegible]	.72
9	Al·Ta	-.06263	-2.24	.71
10	Al·Mo	-.12568	-2.20	.74
11	Mo·Ta	.04489	2.10	.80
	Ao	.16959		

R^2 = 0.930; SEE = 0.2420; INITIAL Z = 25
TOTAL SSQS = 34.46430; EXPLAINED SSQS = 32.06242;
REP SSQS = 0.01955 WITH 8d.f.'s

POSSIBLE OUTLIERS

Number	Alloy	Ka-observed	log Ka observed	log Ka-est.	Std. resid.	Ka-est.
23	31331	12.95523	1.1124	0.4049	2.92	2.541

TABLE VI. - log Ka ESTIMATES AT THREE COBALT LEVELS FOR OPTIMUM Mo (4 wt %) AND Ta (3 wt) LEVELS SHOWING THE OPTIMUM Cr LEVELS AT VARIOUS Al LEVELS INDICATING MINIMUM CYCLIC OXIDATION ATTACK OVER THE PROTOTYPE ALLOY CONTENT SPACE

Al, wt % level	0 wt % Co		5 wt % Co		10 wt % Co	
	Cr level	log Ka est.	Cr level	log Ka est.	Cr level	log Ka est.
3.25	13.0	2.532	14.0	2.803	15.5	2.819
3.50	12.5	2.159	13.5	2.446	15.0	2.479
3.75	12.0	1.780	13.0	2.083	14.5	2.133
4.00	11.5	1.394	12.5	1.715	14.0	1.780
4.25	11.0	1.003	12.0	1.340	13.5	1.422
4.50	10.5	0.6052	11.5	0.9591	13.0	1.058
4.75	10.0	.2017	11.0	.5723	12.5	0.688
5.00	9.5	-.2078	10.5	.1795	12.0	.3118
5.25	9.0	-.6233	10.0	-.2195	11.5	-.07045
5.50	8.5	-1.045	9.5	-.6242	11.0	-.4587
5.75	8.0	-1.472	9.0	-1.035	10.5	-.8529
6.00	7.5	-1.906	8.5	-1.452	10.0	-1.253
6.25	7.0	-2.346	8.0	-1.875	9.5	-1.659

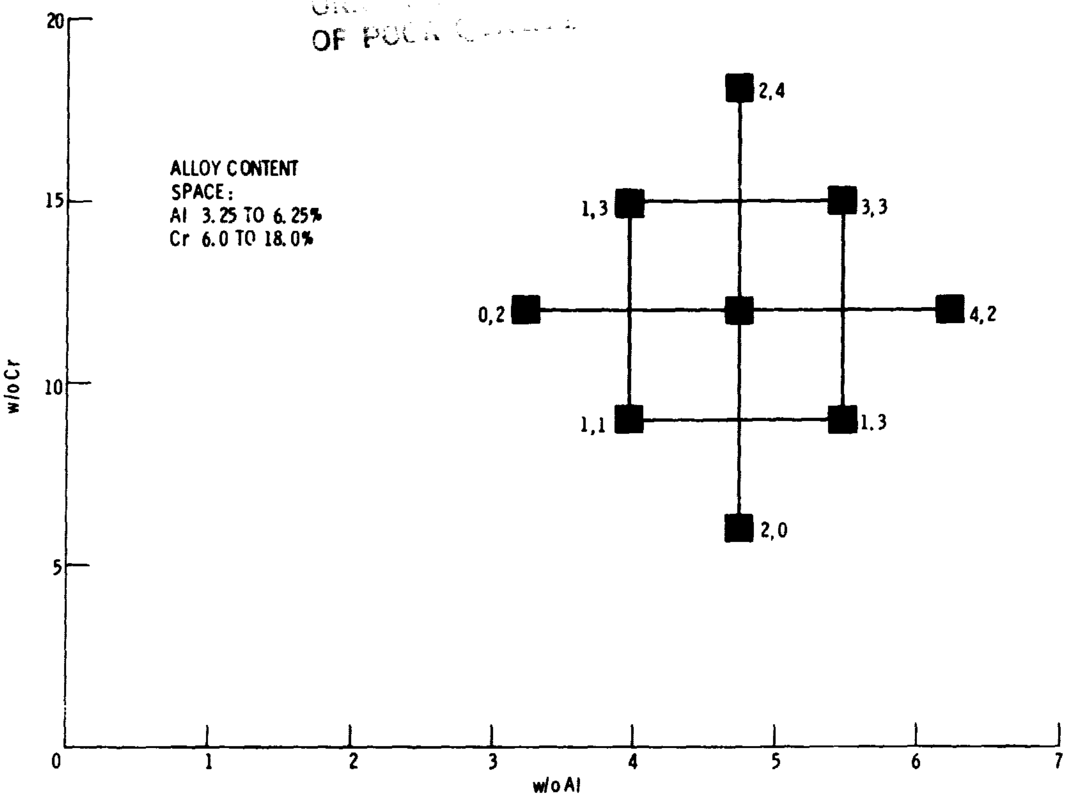

Figure 1. - Illustration of a $(2^n + 2n + 1)$ composite design for $n = 2$ to develop a second degree estimated equation from multiple linear regression.

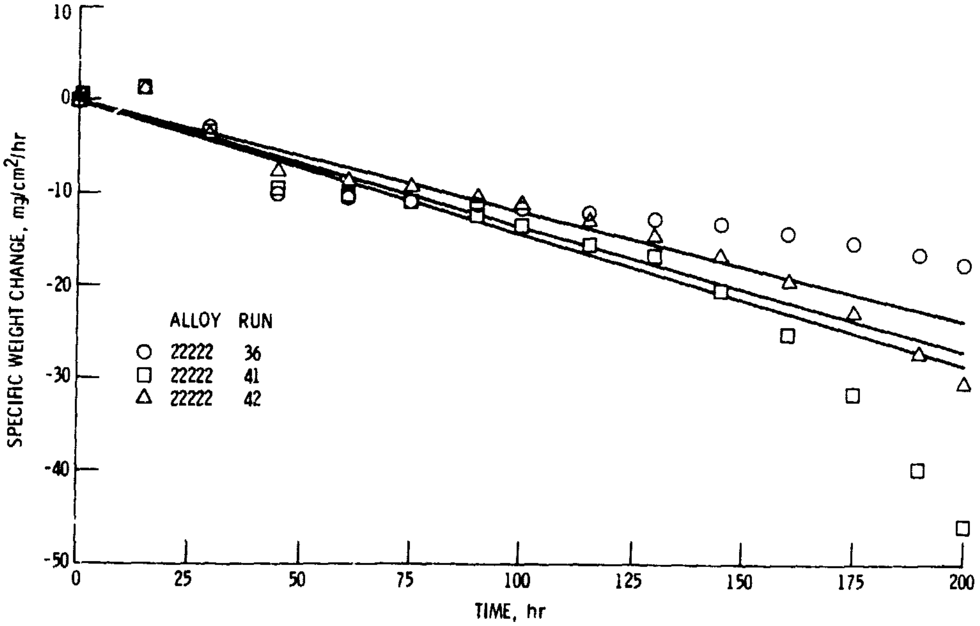

Figure 2. - Cyclic oxidation at 1100 C for alloy (22222) - alloy center.

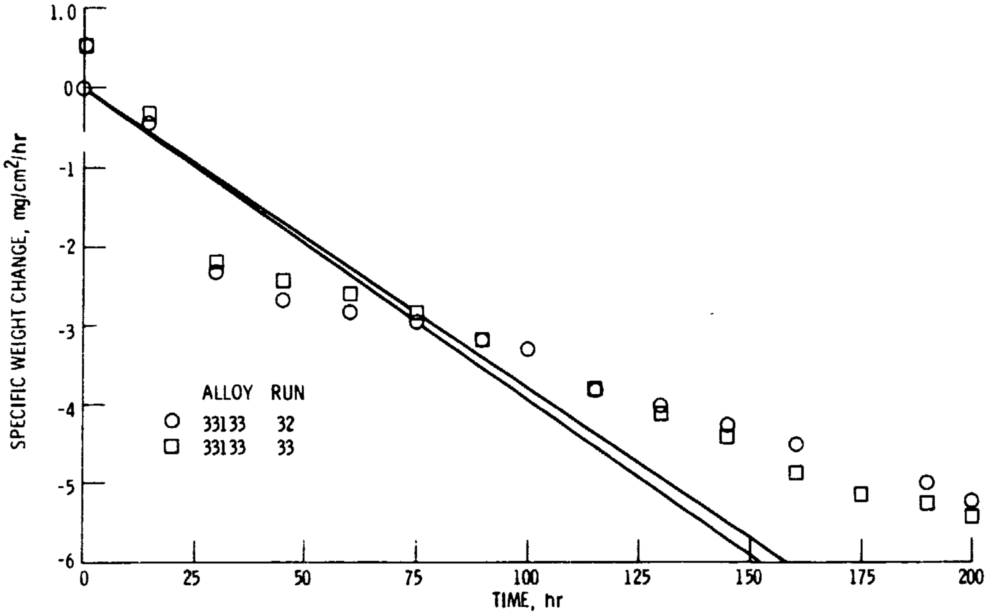

Figure 3. - Cyclic oxidation at 1100 C for alloy (33133).

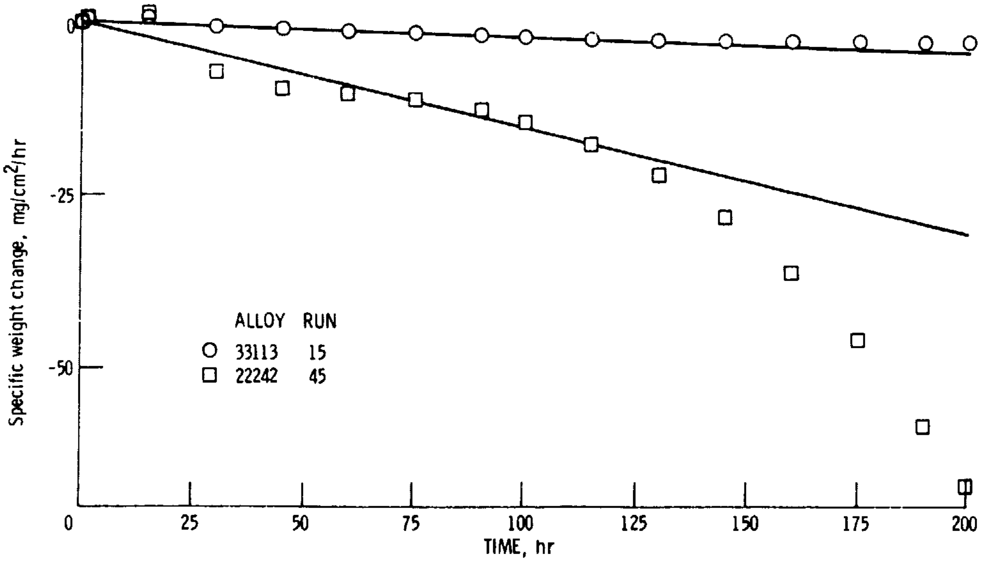

Figure 4. - Cyclic oxidation at 1100 C for alloys (33113) and (22242).

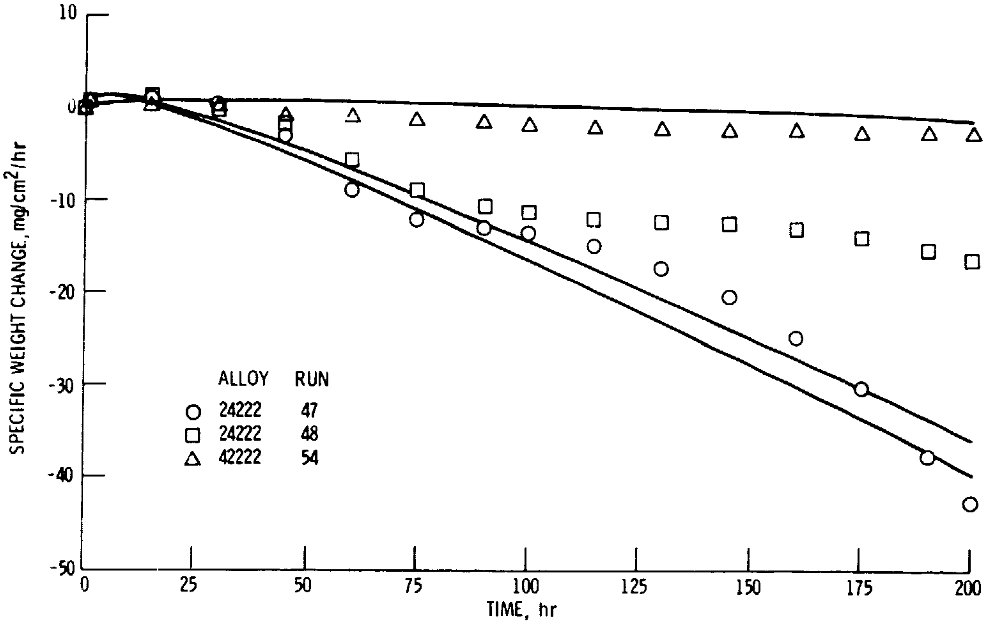

Figure 5. - Cyclic oxidation at 1100 C for alloys (24222) and (42222).

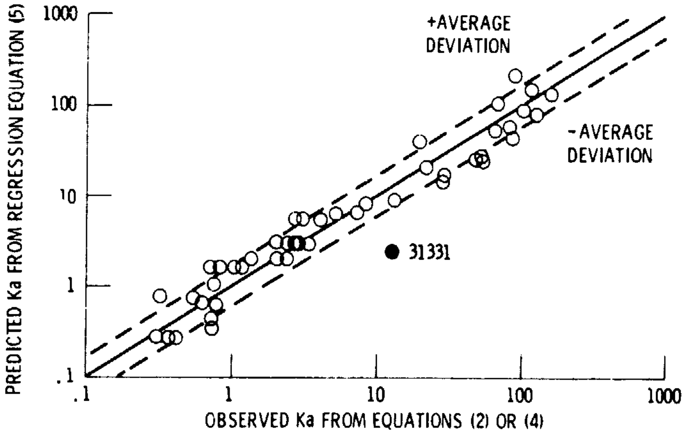

Figure 6. - Correlation between predicted and observed values of Ka. Temperature, 1100° C for 53 alloy samples.