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Comparison of Isothermal with Cyclic Oxidation Behavior of "Cr-Aluminide" Coating on Inconel 738LC at 900 °C

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Abstract A two-step pack cementation technique was used to cover nickel-based IN-738LC superalloy with a Cr-aluminide coating layer. The IN-738LC/Cr-aluminide samples were oxidized at 900 °C for 350 and 700 h, isothermally, and 175 and 350 h, cyclically. Each cycle lasted for 25 h. Effects of the isothermal and the cyclic oxidation on (a) morphology, (b) new-phase formation, (c) weight gain, and (d) oxidation reactions were investigated by scanning electron microscopy, electron dispersive spectroscopy, X-ray diffraction, and weight gain measurements. From results, it was concluded that the oxygen attack was more severe during the cyclic oxidation than the isothermal procedure. Kinetics of the reactions indicated a

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parabolic rate law for the isothermal process, while the cyclic oxidation firstly followed a similar parabolic rate law which was trailed later on by a severe surface spallation.

Keywords Cr-aluminide coating · Isothermal oxidation · Cyclic oxidation · Parabolic rate law · Surface spallation

Introduction

Ni-based superalloys are widely used in hot sections of gas turbines. They resist oxidation in hot environments. Diffusion coating with one or more elements has been used to increase its oxidation resistance [1-3]. One or more elements can be used to achieve best surface coating [4]. Different methods such as chemical vapor deposition (CVD) [5], pack cementation [6], and slurry covering [7] are routine diffusion coating methods. For high-temperature alloys, pack cementation seems the best, due to both simplicity and cost effectiveness [8, 9].

For pack cementation, the specimen is placed within a sealed pack which contains the depositing elements, halide activators, and alumina filler, as shown in Fig. 1. Usual activators are NH₄Cl or NH₄F which are consumed only a little. Under protective atmosphere (usually argon), heat is applied to the pack up to 700 (or as high as 1150) °C. The specimen is kept at this temperature until cementation is completed [10]. Two influential parameters are activity (or concentration) of the coating elements (Al and Cr here) in the source metal and the processing temperature [11]. Three aluminizing processes are generally recognized based on different combinations of metal activity and process temperature: (i) low-temperature high-activity (LTHA), (ii) high-temperature low-activity (HTLA), and (iii) high-temperature high-activity (HTHA). LTHA follows heat treatment above 1000 °C to form NiAl as the most stable phase. This is a two-step process. HTLA



Fig. 1 A scheme view of the equipment used for deposition of Cr-aluminide on IN-738LC superalloy

and HTHA aluminizing processes are done in a single step above 1000 °C to form NiAl coating phase [12].

For protection of substrate from high-temperature oxidation, simple aluminide coatings are used to form adherent Al_2O_3 scale [13, 14]. Aluminide coatings exhibit, however, poor behavior to hot corrosion [15]. Aluminide coating and Al_2O_3 scale both are brittle and sensitive to sulfur. This results in weakening of the oxide–metal interface and ultimate rupture and spallation [16]. Modification of the aluminide coating with chromium results in prevention of internal oxidation of aluminum and helps improving of the hot corrosion resistance [17]. It decreases the depletion of the aluminide coating by retaining a complete layer of α -A1₂O₃ with much lower Al concentration [18]. Pack chromizing with sole Cr does not help, too, because it causes the formation of α -Cr layer or graded Cr-enriched layer [19], both being brittle.

There are two ways for formation of Cr-modified aluminide coatings: (i) codeposition of chromium and aluminum [20] and (ii) two-step pack process which is more effective [21]. If over aluminizing/chromizing is performed by HTLA, a β -NiAl outer layer grows outward with Cr being in the β layer. If over aluminizing is done by LTHA process, Cr-rich phase forms outwards, Cr inclusions form, and growth of the coating occurs inwards. This usually improves the performance of the coating [19].

Although cyclic oxidation causes spallation of the otherwise protective oxide layer, it is more often employed for testing the coating of the superalloys [22]. While coating method substantially affects the oxidation behavior of a superalloy, those alloys which have Cr_2O_3 protective layer on their surfaces are more severely corrosion attacked by cyclic oxidation than the isothermally oxidized samples. Cyclic oxidation of those superalloys which have protective layers other than Cr_2O_3 does not differ considerably from the isothermally oxidized ones [23]. In spite of these observations, no investigation has so far been carried out to compare the oxidation behavior of the cyclic oxidation of the Cr-aluminide-coated IN-738LC superalloy with the isothermally oxidized ones.

 Cr_2O_3 is a less protective scale than alumina at temperatures higher than 840 °C. Since Cr_2O_3 at about 1000 °C sublimates into CrO_3 [23], we picked out 900 °C for oxidation of the samples in this research. Cyclic and isothermal oxidations of Crmodified aluminide coating on the IN-738LC were compared. Thermodynamic and kinetic aspects of oxidation reactions and behavioral changes of the coatings at 900 °C were analyzed by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS), and X-ray diffraction (XRD) analysis.

Experimental Procedures

Substrate

Table 1 indicates the chemical composition of the IN-738LC superalloy used as substrate in this research. Dimensions of the IN-738LC samples were $15 \times 15 \times 3$ mm. They were abraded by abrasive paper SiC No. 1000 for

Table 1	chennea	r compos	nuon or u	10 11 17 50	LC Subst	rate uset	i in uns i	cocaren	(wt/0)		
Element	С	Co	Cr	Мо	W	Та	Nb	Fe	Al	Ti	Ni
wt%	0.11	8.50	16.00	1.75	2.60	1.75	0.90	0.50	3.40	3.40	Bal

Table 1 Chemical composition of the IN738LC substrate used in this research (wt%)

Table 2 Chemical composition of the powders used for pack cementation of the components

Packs	Cr (wt%)	Al (wt%)	Al ₂ O ₃ (wt%)	NH ₄ Cl (wt%)
Powder A	15	0	Bal	2
Powder B	0	10	Bal	1

eradication of the outer layers. Substrates were rinsed with distilled water and ultrasonically degreased with liquid acetone.

Coating

Pack cementation process was used to deposit Cr-modified aluminide onto the IN-738LC substrate. A two-step procedure comprising (i) chromization and (ii) aluminization was employed. The component to be coated was first immersed in powder A of Table 2 at 1100 °C for 5 h and then in powder B of Table 2 at 750 °C for 2 h. The samples were then heat treated. A scheme of the equipment used is shown in Fig. 1.

After weighting, each pack powder was thoroughly mixed by tumbling in a ball mill for 5 h. The component was then inserted into the powder mixture which was filled in a lid-covered alumina crucible. The crucible was placed in an electric tube furnace which allowed flowing of argon at the ambient pressure. Before each step, the pack was demoisturized by holding it at ~150 °C for 2 h. The pack was furnace-cooled after completion of each step. The component was then removed from the loosely embedding pack mixture, lightly brushed, and cleaned by acetone ultrasonication (Fig. 2).

Isothermal Oxidation

An automatic vertical tube furnace equipped with weighing system was used to determine weight gain of the samples against time during oxidation at 900 °C. Samples were placed inside the furnace and were exposed to hot air for 350 and 700 h. Furnace temperature was controlled to within ± 1 % (see Fig. 3). Weight change was recorded continuously to obtain the specific weight gain for the samples.

Cyclic Oxidation

Multiple (175 and 350 times) temperature steps of 900 °C (each lasting for 25 h) were applied to the samples (see Fig. 3). After each step, the sample was cooled down to the room temperature. Cool down period was 30 min. Weight of the samples were measured before and after each cycle. Specific weight gains of the samples were determined in each test.



Fig. 2 Experimental procedure for synthesis, oxidation, and characterization of IN-738LC/Cr-aluminide specimens



Fig. 3 Temperature versus time profiles for isothermal and cyclic oxidation tests at 900 °C under air

Analysis Procedure

The microstructures and chemical compositions of the coating were determined by scanning electron microscopy with X-ray microanalysis (SEM/EDS, Hitachi, Japan; Model: S-3400N). The SEM/EDS analyses were done under high vacuum. Phase

deposition during coating was studied by X-ray diffraction (XRD, Model D/Max 2500PCRigaku, Japan) using Cu Kα radiation (1.5418 Å wavelength).

Results and Discussion

Cr-Aluminide Coating

Figure 4 shows a back-scattered electron (BSE) image of the as-deposited Craluminide coating. A triple-layer structure is observed: (i) a lamellar multiphase inner layer comprising α -Cr precipitates embedded in β -NiA1, (ii) an intermediate layer of β -NiAl with α -Cr precipitates, and (iii) an outer layer with α -Cr precipitates randomly distributed in a matrix of β -NiA1 [21, 23].

EDS analysis of the coating is illustrated in Fig. 5. Its comparison with Inconel 738LC composition given in Table 1 indicates that wt% Cr increases from 16 to 58.86 and Al from 3.4 to 16.79 during pack cementation. The presence of Al and Cr in superalloys prohibits their high-temperature oxidation and corrosion [24]. Low Cr and Al contents are desirable for mechanical strength, creep resistance, and microstructural stability at high temperatures [25]. Boosting Cr and Al surface contents by pack cementation procedure improves, therefore, the oxidation and corrosion resistance without compromising the mechanical strength and creep resistance of the Inconel 738LC superalloy.

Isothermal Oxidation

Surface analysis of the specimens summarized in Fig. 5 indicates that the concentration of chromium and oxygen on surface of the coating enhances by time. During oxidation, Cr diffuses outwards the coated layer resulting in formation



Fig. 4 Cross-sectional representation of the SEM image showing Cr-aluminide coating on the Inconel 738LC substrate



Fig. 5 EDS analysis of the chromium-aluminide coating before and after isothermal oxidation treatments

of a superficial oxide scale comprising bove 90 wt% Cr and oxygen. Al and Ni concentrations in surface of the layer reduce therefore due to Cr rise after 360 h oxidation. This indicates that depth of EDS analysis is confined to the oxide layer and a small portion of the coating exterior adjacent to the oxide layer.

Based on the electron beam effects, the depth of EDS analysis does not exceed the thickness of the coating (i.e., 55 μ m). Applying the power of the instrument (30 kV) into the following equation which has been given by Potts [26], depth of the electron beam effect is obtained less than 10 μ m which is well below the thickness of the coating. The depth of the EDS beam is, therefore, only confined to the oxide scale and a small portion of the coating adjacent to the oxide scale.

$$x\,(\mu \mathrm{m}) = \frac{0.1 E_0^{1.5}}{\rho},\tag{1}$$

where E_0 = Accelerating voltage (keV), ρ = density (g/cm³), and x = approximate depth of electron penetration.

Increasing the oxidation time to 700 h results in somewhat higher Al concentration which indicates better contribution of Al in formation of the oxide scale at longer durations. Cr and Al percentages on the surface of the coating increase continuously up to the level at which protective scale breaks by spallation [27]. At the same time, concomitant diffusion of Cr and Al into the base metal and



Fig. 6 SEM image of the coated surfaces after isothermal air oxidation at 900 $^\circ C$ for a 350 h and b 700 h



Fig. 7 Schematics of oxidation and formation of Cr₂O₃ scale on coated Inconel 738LC alloy

the base metal elements into the coating occurs [28, 29]. EDS analysis shown in Fig. 5 indicates that 700 h is not enough for reaching a maximum critical level for either Cr of Al in the outer layer.

Morphologies of the Cr-modified aluminide coatings after isothermal oxidation at 900 °C for 350 and 700 h are compared in Fig. 6. Both surfaces have oxide scales and cracks, but increase of surface roughness with oxidation time is observable in the figures. Spallation is clearly seen in the sample oxidized for 700 h (Fig. 6b). Image analysis shows that the average scale size increases from 2.6 μ m for 350 h to 4.4 μ m for 700 h oxidation. Large-scale particles seem to favor higher spallation.



Fig. 8 XRD pattern of the samples after isothermal oxidation at 900 °C for a 350 h and b 700 h

Diffusion of Cr^{3+} cations being faster than O^{2-} anions during oxidation causes the formation of a porous Cr_2O_3 oxide phase [30], as illustrated in Fig. 7. As a result, cracks, spallation, and roughening of the surfaces presented in Fig. 6 appear.

XRD results shown in Fig. 8a indicate the formation of Cr_2O_3 on the Cr-modified aluminide coating after 350 h isothermal oxidation treatment. Increase of the oxidation time from 350 to 700 h results in thinning of Cr_2O_3 protective layer by spallation and intensification of γ' -Ni₃A1 peaks, as observed in Fig. 8.

Cyclic Oxidation

Figure 9 shows surface morphology of the Cr-modified aluminide coatings after seven and 14 air oxidation cycles at 900 °C. Progress of the reactions with time was scrutinized by comparison of SEM and XRD images of the samples after seven and 14 cycles of oxidation. SEM images showed increase of the roughness and coating spallation by cycle numbers. A thin scale formed initially on the coated layer. Its thickening was retarded, however, with periodic quench stresses which promoted the spallation. Some micro-cracks appeared at the exterior after 14 cycles of oxidation as highlighted in Fig. 8b.

X-ray maps of the region selected in Fig. 9b are exemplified in Fig. 10. Cr presence corresponds with Cr_2O_3 occurrence which is recognizable in Fig. 11. In a small region of the X-ray maps patterns, Al is evidenced in an insignificant amount, as compared to Cr (Fig. 10). XRD images of the same region indicated short peaks of Al₂O₃, as compared to Cr₂O₃. Figure 11 compares XRD patterns of the samples after seven and 14 oxidation cycles. Higher intensity of the Cr₂O₃ peaks indicates that the amount of Cr₂O₃ in the oxide scale increases after t = 350 h.

For evaluation of the Gibbs free energy of formation of Cr and Al oxides, we assumed that partial pressure of oxygen in the air is 0.2 atm and activity of Cr in the outer layer is one (because Cr particles are distributed in the outer layer of the



Fig. 9 Morphology of the coated surface after cyclic oxidation in air at 900 °C for a 7 cycles and b 14 cycles. X-ray maps illustrated in Fig. 10 belongs to the zone *highlighted* in part (b) of this figure

coating). The activity of Al is also estimated to be 0.35 on the basis of its composition in the outer layer. The Gibbs free energies obtained were

$$2Al(s) + 1.5 O_2(g) \rightarrow Al_2O_3(s) \quad \Delta G = -1677.32 + 0.3466 T \quad (kJ) \quad (2)$$

$$Cr(s) + 1.5 O_2(g) \rightarrow CrO_3(g) \quad \Delta G = -566.89 + 0.2354 T \quad (kJ) \quad (3)$$

$$2Cr(s) + 1.5 O_2(g) \rightarrow Cr_2O_3(s) \quad \Delta G = -1130.11 + 0.2763 T \quad (kJ) \quad (4)$$

$$2Cr_2O_3(s) + O_2(g) \rightarrow 4CrO_2(l) \quad \Delta G = -73.88 + 0.2289 \text{ T} \quad (kJ) \quad (5)$$

$$Cr_2O_3(s) + 1.5 O_2(g) \rightarrow 2CrO_3(g) \quad \Delta G = 3.68 + 0.1944 T \quad (kJ).$$
 (6)

Previous researches have shown that formation and growth of Cr_2O_3 are faster than Al_2O_3 [31]. The former is a good barrier against hot corrosion. However, when specimen is heated up, Cr and then Cr_2O_3 react with oxygen to conduce through Reactions 3–6 [32, 33].

 CrO_3 which is the most prevalent chrome oxide gaseous species may form according to Reactions 3 and 6. Another possible reaction that may lead to the formation CrO_2 is Reaction 7 which is possible when sufficient CrO_3 is present in the system:

$$CrO_3(g) + Cr_2O_3(s) = 3 CrO_2(l) \quad \Delta G = -53.57 + 0.0744 T \quad (kJ).$$
 (7)

Dependence of Gibbs free energy changes of oxidation Reactions 2–7 to temperature is demonstrated in Fig. 12.

In cyclic oxidation, when specimen cools down, the tendency of formation of CrO_2 increases with the lowering of ΔG of Reactions 5 and 7. According to Fig. 12, Cr_2O_3 phase formation is more probable than other Cr oxides. Formation of CrO_3 is also possible as can be seen from Gibbs free energy change of Reaction 3.



O-KA

AI-KA

Fig. 10 Distribution of the elements in the coated specimen after cyclic oxidation at 900 $^{\circ}\mathrm{C}$ for 14 cycles



Fig. 11 XRD results after cyclic oxidation at 900 °C for a 7 cycles and b 14 cycles

Reaction 5 can also proceed at the room temperature to produce CrO_2 phase. Based on XRD results, after 14 cycles, CrO_2 exists in the sample. The formation of CrO_2 on Inconel 738 during oxidation at 900 °C has also been observed by Seal et al. [34]. The formation of CrO_2 at 900 °C in the isothermal oxidation is, however, thermodynamically impossible.

Comparison of Isothermal with Cyclic Oxidation

Specific weight change of the samples at 900 °C during isothermal and cyclic oxidation is illustrated in Fig. 13. From this figure, kinetics of isothermal and cyclic oxidation of the Cr-modified aluminide coating can be explicated: (i) mass gain due to the scale formation and (ii) mass loss caused by protective scale spallation. When the slope of the curve is positive, mass gain occurs; while when the slope becomes negative, mass loss is the case. It is obvious from the curves that the oxidation attack is more severe in cyclic than in isothermal oxidation (see Fig. 13). The specific weight gain curve of the cyclic oxidation firstly shows a scale formation region and then a spallation sections, while the isothermal curve shows no spallation.

Cracking and spallation of the oxide scale are induced during the quenching time of the cyclic oxidation. Considerable specific weight gain rise occurs in the first region of the cyclic curve. Growth of the protective Cr_2O_3 scale would then occur [35]. The highest rate of formation of the scale on the main coating (also observed in the cyclic oxidation curves of Fig. 13) is until the fourth cycle. In region II of Fig. 13, cracking of the oxide scale occurs. One may conjecture the highest portion of the cracking to be caused by structural stresses exerted on Cr_2O_3 and thermal stresses appertained to cooling of the sample. These phenomena also have been observed by previous authors [36, 37].

Scale adaption to deformation is limited. When too much strain rate or stress is applied, scale failure inevitably occurs [38, 39]. In some sections of the weight gain curve, small fluctuations due to the consecutive spallation and rapid reforming of



Fig. 12 Gibbs free energy changes for air oxidation of Cr and Al versus temperature



Fig. 13 Specific weight change of the samples at 900 °C during cyclic and isothermal oxidation

the oxide scale due to repartition of Cr from the underlying coating are observed (Fig. 13). Tensile and compressive stresses are generated at the interface during cooling in the cyclic oxidation [40, 41].

In region III of Fig. 13, the cracked thick oxide scale causes spallation. In this region which starts at $t \ge 300$ h, the weight gain curve begins to descend and coating destruction starts to take place [35, 42]. One reason for destruction of the coating is fall of chromium and aluminum concentrations below a critical level (for Cr, ~16 wt% and for Al, 4–5 wt%) [27]. Cr₂O₃ and Al₂O₃ scales spall during cyclic oxidation due to difference between thermal expansion of the scale with the substrate and their abrupt temperature change which exerts huge stress. Thermal expansion alternations produce residual stresses which facilitate spallation [42].

Another contributing mechanism for spallation is β to γ transformation [43]. Formation of different β to γ phases observed in the XRD patterns is coerced by Alinward diffusion during the oxidation test. Al depletion due to its diffusion from coating towards the substrate and outwards to form protective scale induces β to γ phase transformation. β which has B2 (CsCl) crystal structure changes to γ phase with L1₂ ordering of the martensitic structure [44]. A considerable volumetric change results from this transformation [41] which results in huge stress/strain creation with an undesirable coating destruction.

In isothermal oxidation, a thin Cr_2O_3 scale forms on the coating layer which protects the underlying substrate from destruction. Rapid increase in the specific weight gain occurs due to a widespread Cr_2O_3 creation all over the sample. This protective scale grows little by little causing larger mass gains without coercing large thermal stresses which may cause substantial spallation. No destruction is therefore being observed before $t \geq 350$ h.



Fig. 14 Parabolic weight gain during isothermal and cyclic air oxidation of chromium-aluminide coating layer at 900 $^{\circ}$ C

The data obtained from the isothermal oxidation experiments fit well with the parabolic rate law, as illustrated in Fig. 14. For cyclic oxidation, empirical data follow the parabolic rate law before region III (i.e., $t \le 300$ h). At 350 h $\ge t \ge 300$ h (region III of Fig. 13), spallation occurs with no parabolic law compliance. The parabolic rate constant k_p of the coated layer can be calculated from Eq. 8 [45]:

$$\left(\Delta m/A\right)^2 = k_{\rm p} \cdot t,\tag{8}$$

where $\Delta m/A$ is the specific mass gain, Δm is the mass change, A is the specimen surface area, t is the oxidation time, (h) and k_p is the parabolic rate constant. To follow the parabolic law, square of mass gain versus time must be linear. Closeness of the experimental data with Eq. 8 can be perceived from Fig. 14 which gives the rate constant $k_p^{io} = 6.20 \times 10^{-4} \text{ mg}^2 \text{ cm}^{-4} \text{ h}^{-1}$ for isothermal oxidation of the coated sample. This value for cyclic oxidation is more than twice bigger $(k_p^{co} = 18.28 \times 10^{-4} \text{ mg}^2 \text{ cm}^{-4} \text{ h}^{-1})$. Lower k_p^{io} indicates slower oxidation in the isothermal versus cyclic procedure. This result was confirmed by SEM observations which showed scale spallation in the cyclic oxidation rather than the isothermal procedure.

Implementation of the cyclic oxidation tests was for data collection for prediction of the coating layer performance under severe service conditions. In order to correlate experimental with the real life data, endeavors have been carried out before [46]. Smialek [47] has used a spallation model to describe the cyclic oxidation behavior. The model has been expanded by Lowell et al. [46] who found the number of cycles attaining maximum weight gain (n_{max}) depends on the oxidation rate constant k_p and test duration:

$$n_{\max}\alpha \left(k_{\rm p}\cdot\Delta t\cdot Q_0^2\right)^{-1/3},\tag{9}$$

where Q_0 is a conversion factor for correlating the spallation to the relative weight [48]:

$$Q_{\rm o} = W_{\rm s} / (W_{\rm r})^2,$$
 (10)

where W_r is the total weight of the oxide scale formed during heating (before beginning of the cooling) and W_s is the spalled weight during cooling part of the cycle. From Eq. 10, the amount of Q_0 is obtained to be 0.121 for our system. From Eq. 9, n_{max} for our cyclic oxidation was 12 which agreed well with the experimental number being attainable from Fig. 13.

A comparison of the morphology of the Cr-modified aluminide coating after 350 h isothermal oxidation with 14 cycles oxidation in air at 900 °C is made in Fig. 15. Based on this figure, the average scale size of the isothermal is larger than



Fig. 15 SEM images of the coatings after 350 h air oxidation at 900 °C by **a**, **b** isothermal and **c**, **d** cyclic procedure



Fig. 16 XRD patterns of the coated samples a as-coated, b after 350 h isothermal oxidation, and c after 14 cycles of the oxidation

the cyclic oxidation. Galore stresses created in the cyclic oxidation cause, however, surface spallation before further growth of the scales, as is perceptible from Fig. 15d. More serious surface destruction by cyclic oxidation is also observable in Fig. 15d, as compared to the isothermal procedure.

XRD patterns of the specimens (a) as-coated, (b) after 350 h isothermal oxidation, and (c) 14 cycles of oxidation are shown in Fig. 16. XRD peaks indicate formation of the protective Cr_2O_3 scale on surface of the Cr-aluminide specimens when exposed to the hot air. Chromium can diffuse from the inside layer towards the surface resulting in Cr compounds formation, as inferable from Fig. 16. Both isothermal and cyclic oxidation show Cr_2O_3 peaks intensification.

Figure 16 indicates that the exposition of the as-coated sample to the oxidation condition (whether isothermal or cyclic) results in conversion of the ordered intermetallic β -NiAl (BCC) phase to γ -Ni₃Al (FCC) phase. Although α -Cr participates should exist in the as-coated layer, they are hardly recognizable from β -NiAl embedding phase [49]. As displayed in Fig. 4, the SEM image from Cr-aluminide coating cross section indicates the presence of α -Cr participates embedded in the β -NiAl outer layer.

Conclusions

Cr-modified aluminide coatings were fabricated by a two-step pack cementation process. They were oxidized in air at 900 °C by isothermal and cyclic oxidation. New findings were as follows:

- 1. By isothermal and cyclic oxidation at 900 °C in air, the Cr_2O_3 peaks are intensified and β to γ transformation proceeds.
- 2. CrO_2 forms after 14 heating/cooling cycles.
- 3. Oxidation attack is more severe in cyclic than isothermal oxidation.
- 4. Isothermal oxidation follows parabolic rate law.
- 5. Cyclic oxidation follows parabolic rate law before cycle 12.
- 6. After cycle 12 (Region III of weight gain), spallation starts with parabolic rate law defiance.

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