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**"A STUDY OF SCALE CRACKING AND ITS EFFECTS ON
OXIDATION AND HOT CORROSION"**

FINAL REPORT

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EXECUTIVE SUMMARY

This report briefly summarizes progress during the first two and one half years of a three-year program. One part of the program is a study of the hot corrosion of materials; the other part is concerned with the measurement of stresses in oxide scales and the effects of such stresses on the oxidation behavior of alloys.

The hot corrosion effort has been focussed on SiC, where corrosion rates have been measured in an oxidizing environment as a function of the activity of vapor phase potassium salts (up to ≈ 300 ppm). Potassium dissolves in the normally protective SiO_2 film, causing an increase in the oxidation rate of up to 700 - 800 times that in "clean" environments.

In the study of stresses in oxide scales, we have achieved a major success in having directly measured *in-situ* strains at the oxidation temperature by x-ray diffraction. To our knowledge, such direct measurements have not been reported before. To date, the technique has been applied to Ni/NiO, Cr/Cr₂O₃ and FeCrAlY/Al₂O₃ systems. We feel such data will stimulate new lines of research by: (a) providing a basis for testing new theoretical models of processes that generate stresses in growing oxide films, and (b) providing a foundation for the practical issue of devising improved alloys where the design can now be directly related to the chief degradation process, ie, design to minimize stresses and scale cracking.

Theoretical studies during the past year have attacked the problem of understanding crack initiation and propagation at the metal/scale interface. The elastic-plastic solution for the local stresses about a crack in an anisotropic solid have been obtained and are being applied to the bi-material problem of the oxide/metal interface.

PROGRESS REPORT

I. INTRODUCTION

For many high temperature applications, oxidation (or hot corrosion) is an important mode of degradation of metals and alloys. Degradation mechanisms may be divided into two categories: one dealing with the chemical and transport aspects of scale growth or dissolution, and the other dealing with mechanical aspects such as stresses and scale fracture. Some applications, such as corrosion/erosion, combine both aspects in a complicated manner. Much research has been concerned with relationships between alloy composition and scale growth rates, attempting to identify alloy compositions and growth mechanisms that form compact, slow-growing scales, such as Cr_2O_3 or Al_2O_3 . Nevertheless, in practice a very common mode of scale degradation is cracking and spalling, followed by re-oxidation. Efforts to understand scale stresses and ultimately scale fracture have been hampered by the simultaneous interaction of numerous variables in determining the state of stress. Thus complex issues are involved in both experimental measurements and theoretical models of stresses and fracture of oxide scales.

In this study we have considered both chemical/transport issues (as applied to the oxidation and hot corrosion of SiC and Ni-Cr Alloys) and mechanical issues of oxidation, but the emphasis has been on mechanical issues. In the following sections we will briefly describe the highlights of each of several projects, and where appropriate, will attach pre-prints or reprints of papers that describe in more detail the results of a particular study. The projects are:

- Theoretical Studies of Stresses and Crack Propagation in Oxide Scales
- *In-situ* Measurement of Stresses in Oxidizing Metals and Alloys by X-ray Diffraction
- Thermal Cycling Oxidation and Fracture of Cr_2O_3 Scales on Ni-30Cr
- A Model for Stress Relaxation at Oxide/Metal Interfaces
- Oxidation of SiC in the Presence of Alkali Salt Vapors
- Influence of Alloy Grain Size on the Oxidation Kinetics of a Fine-grained Alumina-forming Alloy

II. THEORETICAL STUDIES OF STRESSES

In the previous annual report, it was suggested that three types of input were essential to the application of theoretical models for oxide scale cracking.

- i) an understanding of substrate deformation mechanisms which appear to provide stress relief during oxidation;
- ii) a determination of unrelaxed thermal and/or growth stresses as a function of temperature and time;
- iii) the application of these unrelaxed stresses to the bi-material interface which contains a crack.

Progress in all three of these issues includes examination of some of the Ni/NiO results described previously (Stout, et al. 1990; Abury, 1988), examination of a prototypical single crystal oxide/metal interface and consideration of recent developments in the bimaterial interface modeling.

II.1. Observations and Calculations in the Ni/NiO System.

Three detailed observations have been noted with regard to developing a comprehensive model of oxide formation in the Ni/NiO system (and perhaps other systems as well). First, the *in-situ* residual strains observed on oxide formation at 900°C fluctuate with time and then reach a steady state that is relatively consistent with a relaxed substrate and oxide scale. Second, the strains on cooling are either near zero (Stout, et al. 1990; Abury, 1988) or slightly compressive. Third, when oxidation was conducted on two grades of nickel, the grade that relaxed the fastest (smallest oxide stresses) also developed the smallest oxide layer after 30 minutes of transient oxidation. This is consistent with the transient oxidation stage of a nickel-base, alumina forming alloy (see section VII, this report) where it was found that the transient oxidation stage was dependent upon the grain size. These three observations all lead to metal substrate relaxation as being a possible rate controlling mechanism in the transient oxidation process.

First, it was assumed that as the oxide initially formed, large stresses developed in the oxide and metal but that some relaxation process in the metal relieves these stresses. At 900°C (1173K) or $T/T_m \sim 0.68$, the dominant creep mechanism is a glide/climb process as originally described by Weertman (1968). With creep strain produced by glide but rate-controlled by climb, Weertman used Hazzledine's analysis of multipoles to finally arrive at, for nickel,

$$\dot{\epsilon}_p \approx a^* D_0 \exp\left(-\frac{q_v}{kT}\right) \left(\frac{\sigma}{\mu}\right)^{3.5} \left(\frac{\sigma\Omega}{kT}\right) \quad (1)$$

where $D_0 = 1 \text{ cm}^2/\text{s}$

$q_v = \text{self-diffusion activation energy} = 277 \text{ kJ/mol}$

$\Omega = \text{atomic volume} = 1.1 \times 10^{-22} \text{ cm}^3$

$\mu = \text{shear modulus} \sim 10^5 \text{ MPa}$

$a^* = 5 \times 10^{20}/\text{cm}^2$

$\sigma = \text{stress}$

For low stresses on the order of $10^{-4} \mu$, this predicts the right creep rates for Ni as observed by Rhines, et al (1970) and Ashby (1973). If stresses on the order of $10^{-3} \mu$ are assumed during oxidation, the creep or relaxation rate is on the order of $5 \times 10^{-3} \text{ s}^{-1}$. This is on the order of the lattice parameter recovery rate ($\sim 5 \times 10^{-4} \text{ s}^{-1}$) which was observed to occur during the transient oxidation stage where large fluctuations in the lattice parameter were observed. In fact, however, the inferred stresses during this stage were on the order of $10^{-2} \mu$. These very large stresses would lead to glide/climb relaxation rates of 100 s^{-1} , much faster than those observed. There are two possibilities:

- i) a slower creep rate controlling mechanism controls relaxation near an oxide/metal interface (not too likely);
- ii) the relaxation process is partly offset by a continued stress build up due to oxide formation in the transient stage.

We are inclined toward the latter view, with the total observed strain (lattice parameter change) being a combination of relaxation and continued oxide growth. In terms of residual strain these are competitive processes, so that the time dependent residual strain, $\epsilon_R(t)$, depends on both the creep kinetics, $\dot{\epsilon}_c$, and the oxidation kinetics, giving

$$\epsilon_R \sim \int [\dot{\epsilon}_c(t) - \dot{\epsilon}_{ox}(t)] dt \quad (2)$$

where $\dot{\epsilon}_c(t)$ for Ni/NiO is glide/climb dependent. Both the creep rate as affected by the dislocation substructure, and the rate of oxidation will be affected by stress, time and temperature. While it is premature to suggest a mechanism, it appears as though the stresses eventually diminished to a small value, giving $\dot{\epsilon}_c \sim \dot{\epsilon}_{ox}$ with the lattice becoming fully relaxed.

The second observation was that residual stresses were near zero or slightly compressive on cooling. From Aubry, et al. (1988) analysis of *ex situ* lattice parameter measurements, it appeared that after 30 minutes of oxidation there was a -20 MPa residual stress in the nickel, whereas after 90 minutes, it was about 15 MPa. Considering the error bars of ± 30 MPa, these are both near zero. If the stresses were fully relaxed during the 900°C oxidation process, the small differences in thermal expansion coefficient ($\alpha_{\text{NiO}} \sim 17.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$; $\alpha_{\text{Ni}} \sim 17 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) used by Aubry, et al. (1988) would give

$$\sigma_R \approx E (\alpha_{\text{Ni}} - \alpha_{\text{NiO}}) \Delta T \approx -87 \text{ MPa} \quad (3)$$

or a near zero residual stress in the nickel.

The third observation was that the nickel grade which relaxed the fastest during transient creep, developed the smallest oxide layer after 30 minutes of oxidation. The polished EO grade developed a -370 MPa stress and a 3 μm thick oxide while the polished E3 grade developed a -460 MPa stress and 5.2 μm thick oxide. The hypothesis is that the lower stress is due to faster substrate relaxation and accordingly smaller stresses in the oxide. The corollary is that slow substrate relaxation leads to high stresses and rapid oxidation. In terms of oxidation rate or rate of weight gain, dw/dt , this becomes

$$\left(\frac{dw}{dt}\right)_{\text{transient}} \propto \frac{1}{\dot{\epsilon}_s} \quad (4)$$

As a test of this hypothesis we used the previous data (described in section VII of this report) on the oxidation of Ni - 2.5 Fe - 16.2 Cr - 4.7 Al - 0.1 Si - .02 Y at 1150°C. This temperature gives $T/T_m \sim 0.82$ with the controlling creep mechanism in the substrate being Nabarro-Herring, giving

$$\dot{\epsilon}_s \approx \frac{7\sigma D_v b^3}{kTd^2} \quad (5)$$

where D_v is volume diffusivity and d is grain size. With the assumption that this creep rate is the substrate relaxation rate, Eqs. (4) and (5) give

$$\frac{dw}{dt} \propto \frac{1}{\dot{\epsilon}_s} \propto d^2 \quad (6)$$

Thus, the rate of weight gain should be proportional to the square of the grain size. This is significant since it was originally thought that rapid diffusion down grain boundaries would assist the transient oxidation process. This would lead to short time oxidation kinetics being increased by fine grain structures[†]. Equation 6 predicts just the opposite as was observed by the experimental data and illustrated in **Fig. 1**. The tentative conclusion then is that the transient oxidation stage is inversely proportional to the rate of substrate relaxation. Note that for the steady-state oxidation process, no effect of grain size was observed. This is consistent with the substrate being fully relaxed and the steady-state plateau in metal lattice parameter observed after a transient stage.

A.2. Single Crystal/Oxide/Metal Interface.

A microcrystalline oxide tends to grow on a metal substrate with relaxation of the substrate. A study of such interfaces without relaxation would be useful except that it is too difficult to develop a well-defined thickness of oxide at low temperatures. It is easier to develop a polycrystalline/single crystal interface of a sputter deposited metal on a single crystal oxide substrate. While not the same, there are analogous issues of relaxation, thermal expansion mismatch and anisotropic elasticity which can be addressed. For that reason, we selected Cr films deposited on sapphire (Al_2O_3) single crystals since these were commercially available. It is noted that the analogous oxidation interface would be produced in some Ni-Cr-Al alloys where Al_2O_3 is the preferred oxide former. The importance of this is that very high stresses have been developed in chromium films deposited on glass, aluminum or stainless steel substrates (Hu and Evans, 1989). Here, it was found that film cracking proceeded with a $K_{Ic}^f \sim 2.8 \text{ MPa} \cdot \text{m}^{1/2}$. We deposited a 1600Å thick film with no film cracking. However, the stress intensity for interface cracking is

$$K_I = 0.98 \sigma_f \sqrt{h}$$

where σ_f is the film stress and h is the film thickness. For the film stresses of about 2000 MPa, this only gives a K_I value of 0.78 $\text{MPa} \cdot \text{m}^{1/2}$, insufficient for film cracking. We are in the process of analyzing such films for residual stress and the rate of relaxation in such

[†] The additional possibility is that in these alloys it is solute diffusion down grain boundaries which is enhanced leading to protective oxides and thus enhanced oxidation resistance in fine-grain structures.

oxide/metal systems, important to film cracking mechanisms at ambient temperatures. This issue is addressed in additional detail in the proposed work.

II.3. Analysis of Elastic-Plastic Stress States

One goal has been accomplished this last period and two alternatives are being explored for modeling the bi-material interface problem. With regard to the anisotropic elastic-plastic problem, various types of anisotropic slip have been considered and analyzed. Attempting to apply this to the bi-material interface is quite difficult. Two approaches are being explored, one using a combined discretized dislocation analysis with finite element analysis to satisfy boundary conditions and the other a surface Green's function approach. At this stage the latter is only elastic.

II.3.1. Computational Results of the Stress State Ahead of a Crack Tip

In this "elastic-plastic" analysis, the sample material is an iron crystal with elastic constants of $C_{11} = 24.2$, $C_{12} = 14.65$ and $C_{44} = 11.2$ in units of 10^4 MPa and the crack length $a = 0.01$ m. All of the discretized superdislocations are assumed straight and parallel to the z-axis, and also lie in a plane which cuts the xy plane in a slip trace at an angle θ to the x-axis. The dislocation can move in this plane in a direction which makes an angle ϕ with the z-axis. All of the parameters used in the computation scheme for various K_I are listed in Table 1.

The elastic simulations from this model were compared with the analytical elasticity solutions (Hellan, 1984); as expected, no difference was found. It was found that significant regions of calculated elastic stress far exceeded 100 GPa, which is unacceptable for equilibrium since this exceeds the theoretical strength by a factor of three. The elastic-plastic stress contours were also compared with corresponding elastic stress contours. No obvious differences were found at a distance about 1 mm away from the tip which is also consistent with the continuum model since the plastic zone size was ≤ 1 mm. It should be pointed out that a reasonable agreement with a continuum small-scale yielding solution was also obtained to within about $1 \mu\text{m}$ of the crack tip.

On the other hand, the stress state very near to the crack tip is at large variance with either the elasticity or the continuum elastic-plastic results in a number of ways. First, the present analysis removes the stress field singularity (at the crack tip). Instead of the highest tension point, the stress at the crack tip became slightly compressive due to dislocation shielding. The result of a completely shielded crack tip is unexpected although anticipated, in the context of the Rice-Thomson model (Rice and Thompson, 1974). As is seen in Table 1, this local stress maximum varies between 3200 and 148,000 MPa which brackets

the actual theoretical stress of about 40,000 MPa. The high value is thought to be an artifact of core overlap due to the superdislocation of $36 b_0$ at 70\AA from the crack tip. As that was not the case in the others, the importance of the factor of eight difference in maximum stress is thought to be important to the understanding of how inverse dislocation pile-ups from the crack tip lead to a local failure criterion. Of course, this would also be applicable at a bimaterial interface where slip-bands from the metal side present a local stress concentration to the oxide that is forming. More details on this anisotropic, elastic-plastic model are presented in a PhD thesis, "Stress States Near Bi-Material Interfaces," by Mirng-Ji Lii, University of Minnesota, 1989.

II.3.2. Extension to Bi-material Interfaces

The first attempt was to take the discretized dislocation solution for the elastic-plastic material and couple it to an interface where the material on the other side is elastic. For the elastic side, the boundary value problem could be solved by finite element analysis (FEA). This, then, represents a "Finite Element Analysis for Bi-Material Interfacial Bonding with Crack-Dislocation Interaction." Some progress was made on this problem with an A/B interface by using the discretized dislocation solution in A and FEA in B. The boundary conditions on the interface are connected by

$$\underline{u}_{\text{int}} A(x) + \underline{u} A(A) = \underline{u} (B)$$

$$\underline{\sigma}_{\text{int}} A(x) + \underline{\sigma} A(A) = \underline{\sigma}_{\text{int}} (B)$$

where $\underline{u} A(A)$ and $\underline{\sigma} A(A)$ are from the original Atkinson solution for the displacements and stresses in material A, $\underline{u}_{\text{int}} A(x)$ and $\underline{\sigma}_{\text{int}} (x)$ $\underline{\sigma}_{\text{int}} A(x)$ are auxiliary solutions required by interactions across the interface and $\underline{u} (B)$ and $\underline{\sigma} (B)$ are solutions in material B, as satisfied by FEA. There is a major problem because of interactions across the interface and to explore a possible solution, a special imaginary "bonding" or "transformation layer," TL, has been invoked. The importance of this TL is that A and B have no dislocation-crack interaction within it which allow an appropriate numerical approximation and satisfaction of the boundary value problem. While the FEA and discretized-dislocation software for such a problem is in place, we are concerned that the transformation layer will lead to artifacts in the local region where the stresses are most important to interfacial decohesion and oxide-

scale cracking. Before embarking along this path, it is first more realistic to compare such a solution method to an A/B interface problem which just involves anisotropic elasticity.

In the previous annual report, it was suggested that the oscillatory stresses of the traditional elastic bi-material interface problem prevent a good description of the stresses very near to a crack tip at the interface. Very recently, a surface Green's function approach has been applied to the interface problem by Gao (1990). This uses a long range distribution of mismatch dislocations along the interface. This requires a core cut-off radius, r^0 , to avoid the oscillatory nature of the stresses near the crack while reserving the long range mismatch effect outside this non-linear zone. While the first order solution recovers the exact oscillatory solution of Rice and Sih (1965), it has the promise of being more easily extended to anisotropic A/B interfaces using anisotropic surface Green's functions as derived by Lothe and Barrett (1976). If success is obtained by this method, then a solution for the elastic stresses in anisotropic elastic media across an interface might be possible. Presently, only the linear elastic solutions for isotropic materials are readily available (Suo and Hutchinson, 1990).

III. EXPERIMENTAL MEASUREMENT OF SCALE STRESSES

Progress in the first year of this grant was focussed on two objectives. The first was to evaluate the sign and magnitude of the residual elastic strain that develops across the interface between a metal substrate and an attached oxide. The oxide forms at elevated temperature but upon cooling, very significant residual stresses can develop. We chose Cr/Cr₂O₃ as our model system and x-ray diffraction as the basic technique for evaluating the residual strain in both the oxide and the Cr substrate. The results of this study demonstrated in-plane compressive stresses in Cr₂O₃ of several thousand MPa, and in excess of that expected from a calculation of lattice mismatch between the oxide and the metal due to cooling from high temperature (Stout, et al. 1986). We concluded that growth stresses developed at elevated temperature during oxide formation could make a significant contribution to that observed residual stress at room temperature.

The second objective was to design a procedure and an experimental apparatus by which the x-ray diffraction technique could be directly applied at elevated temperature such that the conclusion drawn above could be experimentally verified. To our knowledge, this experiment had never been done in the context of the intended application. Rapid progress had been made in that direction by the end of the first year.

The major accomplishment in the second year of this grant was to demonstrate, by direct experiment, the existence of significant growth stresses in a metal/oxide scale system at high temperature. The experimental procedure which we designed allows high

temperature X-ray diffraction measurements to be made during oxide growth. Briefly, the experiments utilize the interplanar lattice spacings of crystalline alloys and their attached oxides as strain gauges. An unoxidized alloy is initially heated to elevated temperature in an inert atmosphere, and, of course, its lattice expands. The interplanar spacings of the lattice are measured by X-ray diffraction as a function of temperature. After the alloy is fully equilibrated and its interplanar spacings remain unchanged, preheated oxygen is introduced into the furnace at temperature. The alloy oxidizes isothermally and the elastic response of the alloy substrate to the developing scale is monitored by the diffraction technique.

Figure 2 illustrates a typical experimental run on a 25 μm thick Ni foil, beginning at room temperature (RT) (Stout, et al., 1989). The data points on the upper straight line represent the metal strain (in percent) due to thermal expansion to 900 $^{\circ}\text{C}$, in an inert atmosphere in order to minimize oxidation. Once thermal equilibrium has been established at 900 C, oxygen is introduced and NiO begins to grow on the foil. The response of the foil to that isothermal oxidation process is shown by the strain data in the inset of **Fig. 2**. An initial compression is followed by an apparent relaxation and that pattern is repeated 3 more times in a little more than 2 hours after oxidation commenced. Thereafter, the strain stabilizes at the thermally expanded value (about 1.36 % strain relative to RT) and does not change until cooling is initiated. In this particular experiment, there was no measureable residual strain (other than thermal strain) after the foil was cooled with its oxide scale intact to room temperature. In other experiments, the metal strain due to oxidation is gradual with no evidence of the oscillating behavior illustrated in **Fig. 2**. In these cases, significant residual stress is evident at RT.

The two types of behavior just described have been experimentally confirmed in additional runs and the appropriate checks have been made to eliminate the possible effects of sample rotation and/or crystallite rotation during the oxidation process. We conclude that the metal behavior at high temperature is responding to the developing oxides. The details of that response are not as yet understood, but we suspect that the oscillating strain behavior at high temperature may be due to successive relaxations of accumulating metal strain, e.g., by cracking, as the oxide grows. Such behavior seems to minimize the final residual stress. The major accomplishment in the third and final year of this grant was to refine our procedures for measuring high temperature growth stresses and to apply these procedures to different materials.

Figure 3 illustrates the results of an experiment on NiCrAlY, oxidized at 1000 C for 24 hours. The thermal history shown by the open symbols includes cooling from the oxidation temperature back down to room temperature and an additional period of 20 hours

in order to evaluate further stress release. The corresponding strain history as recorded in the (200) lattice spacing of the alloy is shown by the closed symbols. The linear expansion of the lattice during heating corresponds to previous, independent results. Upon oxidation, however, the alloy substrate gradually goes into compression relative to the thermally expanded but otherwise unstrained state. This strain accumulates over the oxidation period and then is apparently preserved as the major component of the residual strain after cooling is complete. The thermal contraction due to cooling is indistinguishable, except in sign, from the expansion due to heating. Thus the alloy residual strain is in a state of slight compression relative to the initially unstrained, room temperature lattice.

The relative strain of the alloy throughout the thermal cycle just described can be determined because the strain-free state could be established prior to the experiment. This is not the case for the attached oxide scale. The strain-free state of the oxide can only be obtained after the experiment, once it is detached from its substrate. Because the amount of oxide is so small, we have developed a procedure in the last several months by which the oxide is separated from its substrate, thereby relaxing any residual stress that may be present. Briefly, the substrate and oxide together are placed in the top of a finely tapered glass capillary and the metal is dissolved away with a bromine solution. After dissolution, the solution is repeatedly decanted and the oxide flakes are washed. Then the released oxide is allowed to settle into the finest part of the capillary. That end of the capillary is then broken off and placed in a Debye-Scherrer X-ray camera for precise lattice parameter measurements.

Our initial results from this procedure shows that the scale that develops on NiCrAlY at 1000 C is pure α -Al₂O₃, and its lattice parameters are indistinguishable from those of an independent standard. This means that there can be no compositional effects during oxidation or cooling that could have misled us in our interpretation of the observed changes.

IV. THERMAL CYCLING OXIDATION AND FRACTURE OF Cr₂O₃ ON NI-30CR

Nickel-30Cr is a simple alloy that can serve as a model for oxidation and corrosion processes on complex, Ni- base superalloys. Nickel-30Cr reliably forms a Cr₂O₃ scale during high temperature oxidation, but the scale cracks and/or spalls on cooling to ambient temperatures. The oxidation of Ni-30Cr alloy was studied under thermal cycling conditions to examine the scale fracture process. In a typical experiment a sample was heated rapidly to the oxidizing temperature (1000°C) in O₂ and held isothermally for some time to grow a Cr₂O₃ scale. Then a series of three thermal cycles (isothermal temperature -

cool - return to isothermal temperature) with increasing ΔT 's of 100, 200 and 300°C were imposed, culminating in cooling to room temperature. Using acoustic emission (AE) we monitored the occurrence of scale cracking during these experiments. Typically, no significant cracking was observed during the isothermal regime, but extensive cracking and spalling were observed during the cool down and occasionally during the thermal cycling. From these experiments we have measured the ΔT to initiate extensive scale cracking for scales of different thickness (grown at 1000°C for different times) and for scales of the same thickness, but grown at different temperatures. ΔT is a measure of the thermally induced stresses owing to the different thermal expansivities of the metal and oxide. This stress is superimposed on any pre-existing stresses formed during the isothermal growth period. Thus, to a first approximation, the net stress at scale fracture, S , may be represented as:

$$S = A(\text{scale thickness}) - B(\text{time, temperature}) + C(\Delta T \text{ thickness})$$

where "A" represents the growth stress and is a function of scale thickness and growth mechanism, "B" represents the relaxation of the growth stress owing to creep of the substrate and/or scale and "C" represents the thermal stress. C is well characterized in the present experiments, and B may be estimated from our model for stress relaxation* (see below), but, unfortunately, A is not known. The evolution of stresses with time in growing scales is quite complex and has not been properly modelled to date.

The results of our study showed that thick scales grown at 1000°C cracked at a smaller ΔT than thin scales. This suggests that either (a) the growth stress increases with scale thickness or (b) the stress to fracture a thick scale is less than that for a thin scale. Inference "a" is more likely. For a given scale thickness grown at two temperatures (800 vs 1100°C), a smaller thermal stress was needed to fracture the scale grown at the lower temperature. This result is probably due to less stress relaxation, and hence a larger net growth stress, at the lower temperature. Clearly, other factors, such as the microstructures of the scales, could also vary in these tests and could affect the fracture stress. A draft paper on this work is attached.

V. A MODEL FOR STRESS RELAXATION AT OXIDE/METAL INTERFACES

* J.J. Barnes, J.G. Goedjen and D.A. Shores, (1989) "A Model for Stress Generation and Relief in Oxide/Metal Systems During a Temperature Charge," *Oxid. of Metals*, **32**, 449-469.

Theoretical calculations by Gerberich and student and residual strain measurements on Cr_2O_3 scales at room temperature by Stout and student demonstrated the existence of quite large stresses in the oxide and lower, but still substantial stresses in the metal substrate at the oxidation temperature. For many alloys, imposing a tensile stress of such a magnitude would cause creep at the oxidation temperature, and consequently relaxation of growth stresses by alloy creep seems plausible. We have devised a model to account for stress relaxation owing to creep of the substrate and/or of the oxide. For the systems we have considered, (Cr_2O_3 formed on Ni- base alloys or on Cr) the creep rate of the oxide is thought to be insignificant, but creep of the substrate can be quite significant, depending upon the choice of alloy and temperature. Because there is no accepted model for isothermal stress generation due to oxide growth, we have applied our model only to thermally-induced stresses during cooling. According to our model, stress relaxation does occur during cooling, and the magnitude of the relaxation depends on the cooling rate, temperature and creep properties of the materials (eg, Ni- 30Cr relaxes more than MA-754, a creep resistant commercial alloy, for a given slow cooling rate). An example calculation for Ni- 30Cr is shown in **Fig. 4**. A paper describing these calculations has been published: Barnes, et al., 1989, and a preprint is attached.

VI. OXIDATION OF SiC IN THE PRESENCE OF ALKALI SALT VAPORS

The purpose of this study is to characterize the oxidation response of SiC when the environment contains small concentrations of alkali salt vapors. The oxidation of SiC in "clean" environments, eg. pure O_2 , produces a SiO_2 scale which is very protective at high temperatures. On the other hand, alkali vapor species can react with the SiO_2 and modify its properties. In our studies, potassium has been incorporated into the SiO_2 scale formed on sintered α -SiC, and the potassium has drastically lowered the scale viscosity and increased the rate of transport of oxidant across the scale to the SiC surface. As a consequence, we have observed oxidation rates as much as 700-800 times higher when the environment contained a few hundred ppm (up to ≈ 325 ppm) of a potassium salt than that for "clean" oxidation. Furthermore, the oxidation kinetics changed from parabolic to linear with the addition of potassium. A plot of the oxidation/corrosion rate, as a function of activity of potassium salts in the gas phase, is shown in **Fig. 5**. A paper describing this work has been submitted for publication and a preprint is attached.

As a closing effort on this study, we are considering some schemes which are intended to reduce the rate of oxidation in alkali contaminated environments.

VII. INFLUENCE OF ALLOY GRAIN SIZE ON THE OXIDATION KINETICS OF A FINE-GRAINED ALUMINA-FORMING ALLOY

The steady-state oxidation rate of alumina-forming alloys is known to be controlled by grain boundary diffusion of oxygen through the scale, but the rate controlling factors during the transient stage of oxidation are less well understood. It has been observed that rapid diffusion of alloy solute via grain boundaries during this transient stage can alter the oxidation rate and resulting oxide morphology. The purpose of this project was to study the effect of alloy grain size on short and long term oxidation kinetics. The materials studied were a plasma-sprayed nickel base alumina-forming alloy of composition Ni-2.5Fe-16.2Cr-4.7Al-0.1Si-0.02Y and Cabot 214 (supplied by Haynes International), a wrought alloy of nominally the same composition.

The plasma-sprayed alloy with as-received grain size of 1.4 μm was heat treated to obtain a range of grain sizes from 1.4 to 32 μm . The Cabot 214 alloy had an as-received grain size of 65 μm . Oxidation kinetic were measured at 1150 $^{\circ}\text{C}$ in oxygen by TGA. During the transient oxidation stage, the rates of oxidation decreased with decreasing grain size, and this was attributed to increased grain boundary diffusion of Al to the metal/scale interface, which promoted selective oxidation of Al. (See section A1 for an alternative interpretation.)

Acoustic emission experiments were carried out to obtain information about differing tendencies toward scale cracking and spalling. No significant amount of acoustic activity was detected during the heating stage, transient stage, or isothermal oxidation period, regardless of alloy grain size. Nevertheless, some cracking or spalling in the initial stages, where the oxide is relatively thin, might have been below the threshold detection limit of the system. A substantial amount of acoustic activity was observed on cooling from the oxidation temperature to room temperature, but no correlation with alloy grain size was found. This behavior suggests the stress-related behavior is established by the steady state oxidation process, which is controlled by transport through oxide grain boundaries. A draft of a paper (prepared by the graduate student) describing this study is attached.

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CURRENT AND PENDING FEDERAL SUPPORT**D.A. Shores**

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J.H. Stout

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W.W. Gerberich

DOE	Micromechanics of Brittle Fracture: STM, TEM and Electron Channeling Analysis	\$229,691	7/1/90-6/30/93
ONR	Microstructure and Texture Control of Fatigue in Hydrogen and Marine Environments	\$251,288	3/1/89-2/29/92

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Table 1

Parameters for Discretized Superdislocation Model
 ($\phi = 54.7^\circ$ for all cases, mini-slip band and plastic zone at the same slip angles)

Case Number	T_{22} (MPa)	Stress Peak (MPa)	σ_{fric} (MPa)	L's positions (μm)	b_i strength ($b_o = 2.5\text{\AA}$)	θ_y or θ_m (degrees)
(a) (suggested by Atkinson and Clements)	90.2	25000	100.2	0.028	$36b_o$	45.0
				0.376	$36b_o$	45.0
				1.238	$36b_o$	45.0
				2.596	$36b_o$	45.0
				4.590	$36b_o$	45.0
			300.0	$10600b_o$	45.0	
(b) ($\bar{2}11$)[111] slip system	89.8	148000	100.4	0.007	$36b_o$	26.56
				0.170	$36b_o$	26.56
				0.676	$36b_o$	26.56
				1.671	$36b_o$	26.56
				3.343	$36b_o$	26.56
				115.7	$6350b_o$	26.56
(c) ($\bar{1}12$)[$\bar{1}\bar{1}1$] slip system or ($\bar{1}10$)[111] slip system	89.9	17900	100.2	0.042	$36b_o$	45.0
				0.553	$36b_o$	45.0
				1.748	$36b_o$	45.0
				3.558	$36b_o$	45.0
				6.156	$36b_o$	45.0
			405.0	$11350b_o$	45.0	
(d) ($\bar{1}21$)[111] slip system	90.0	4700	100.5	0.126	$36b_o$	63.43
				1.073	$36b_o$	63.43
				2.753	$36b_o$	63.43
				5.119	$36b_o$	63.43
				8.474	$36b_o$	63.43
				457.0	$12990b_o$	63.43
(e) (011)[$\bar{1}\bar{1}\bar{1}$] slip system	90.0	3200	100.0	0.127	$36b_o$	90.0
				0.875	$36b_o$	90.0
				2.222	$36b_o$	90.0
				4.180	$36b_o$	90.0
				6.969	$36b_o$	90.0
				170.0	$10450b_o$	90.0

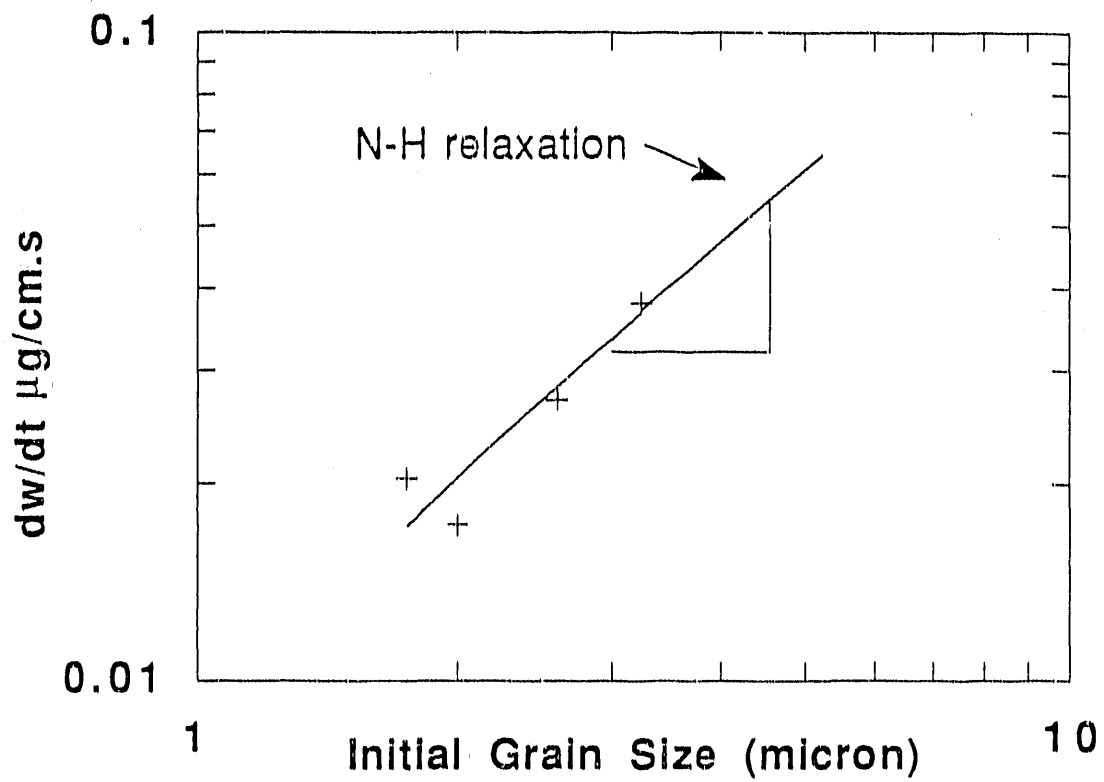


Figure 1. Correlation of transient oxidation rates with alloy grain size.

Oxidation Behavior of Nickel At 900°C

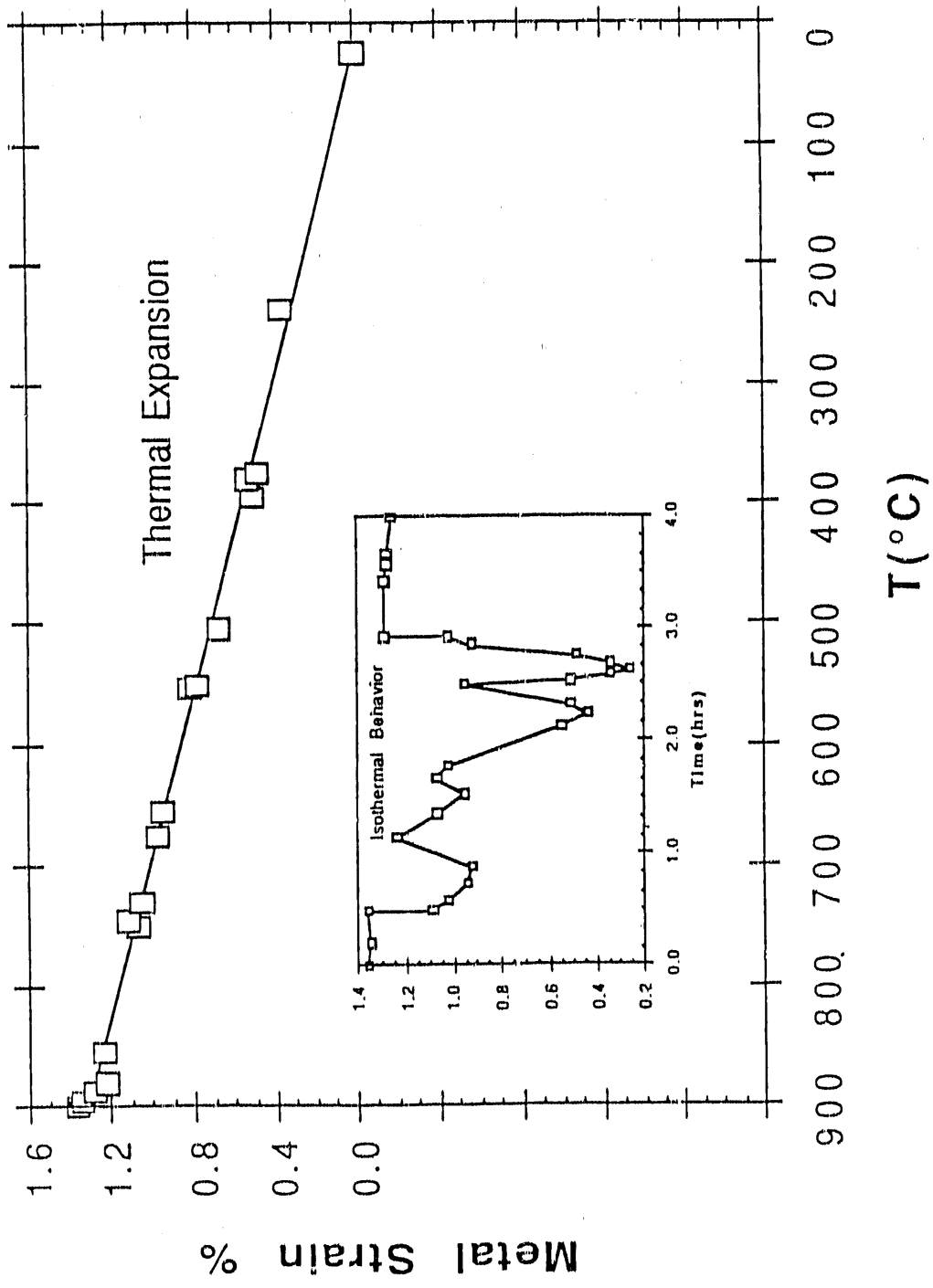


Figure 2 Results of *in-situ* X-ray diffraction measurements of strains on Ni owing to oxidation.

Oxidation of NiCrAlY

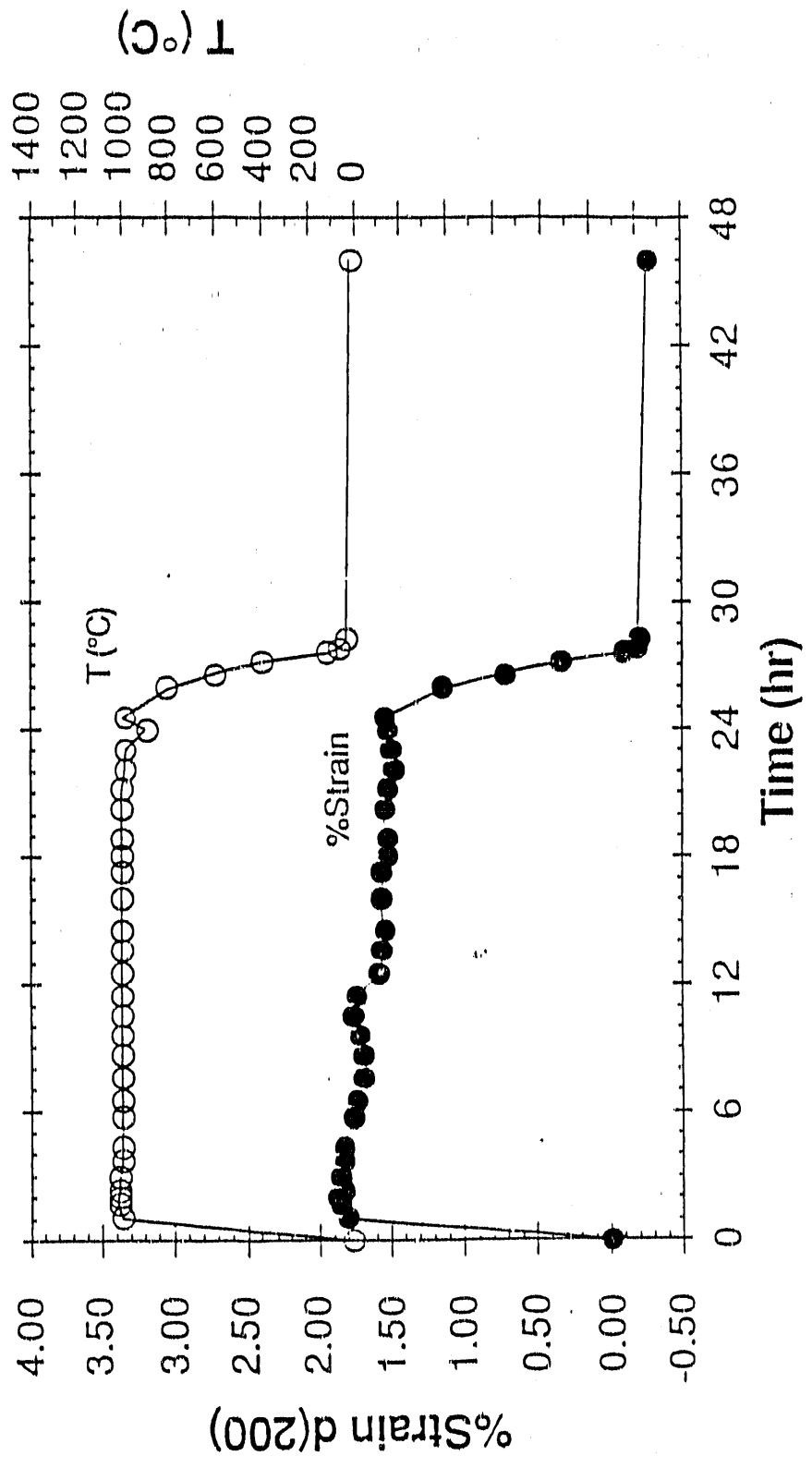


Figure 3 Results of *in-situ* X-ray diffraction measurements of strains on Ni-Cr-Al-Y alloy owing to oxidation at 1000°C.

Ni-30Cr / Cr₂O₃

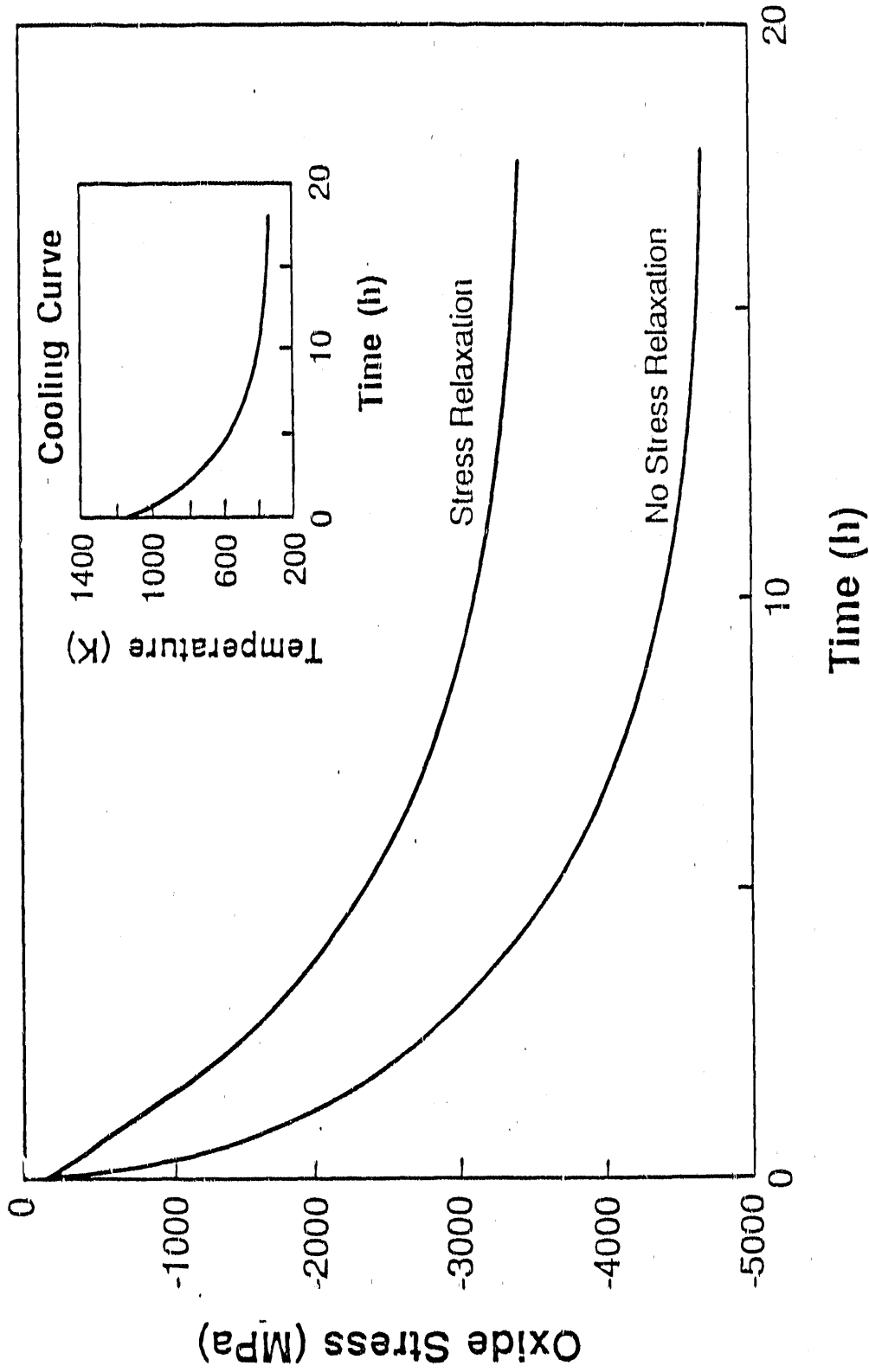
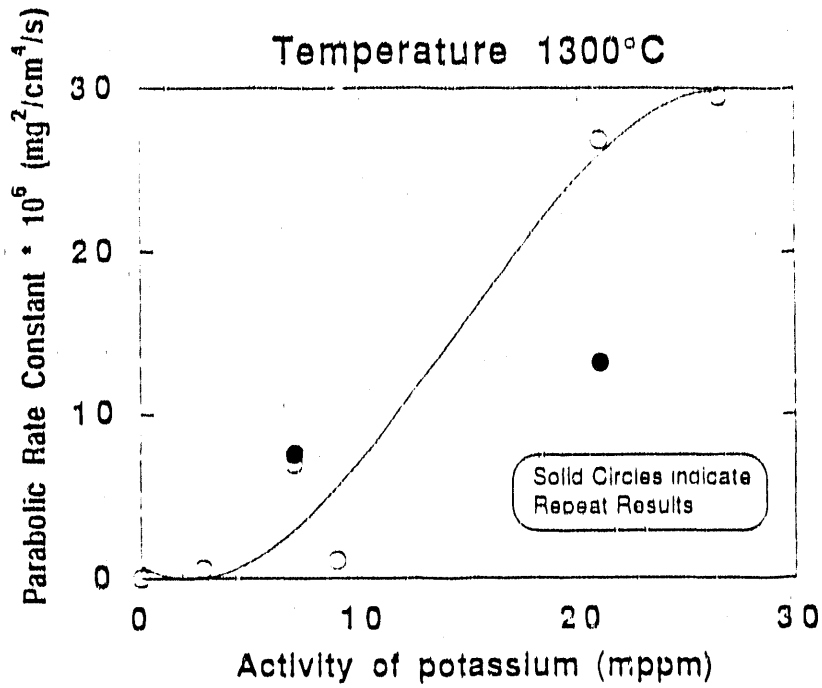
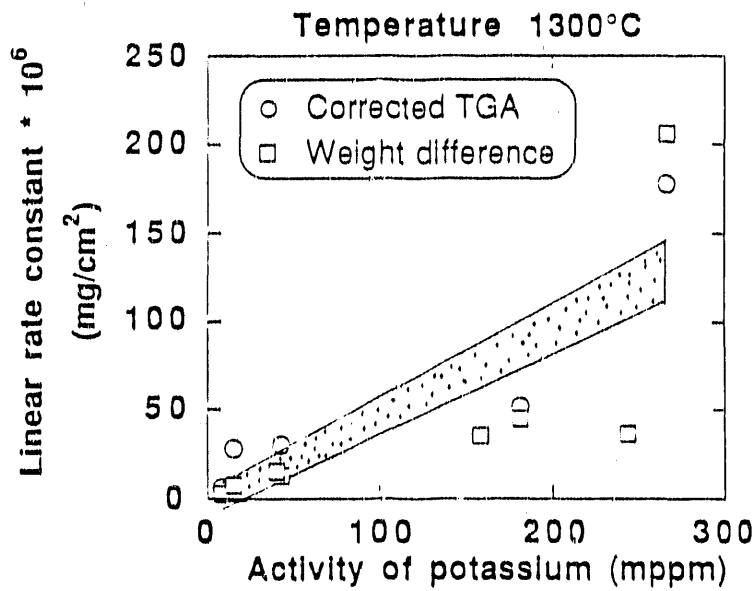


Figure 4 Calculated thermal expansivity stresses on cooling slowly to room temperature allowing for substrate creep ("relaxed") or disallowing substrate creep ("unrelaxed").



Parabolic rate constant as a function of potassium salt vapor level for dry CO₂-O₂ (9:1) gas mixture at 1300°C.



Linear rate constant as a function of potassium salt vapor level for CO₂-O₂-H₂O gas mixture at 1300°C with various pH₂O.

Figure 5 Corrosion rates for the oxidation of SiC as a function of potassium salt vapor level.

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