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MECHANICAL PROPERTIES OF CRYSTALLINE SOLIDS

by

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ABSTRACT

The deformation model for non-elastic deformation in the grain matrix based on a mechanical equation of state was verified by comparing the predictions of the model with experimental data. The data of Type 316 stainless steel and nickel were used and were obtained in load relaxation and anelasticity tests. The same model was found to be successful in describing in-reactor creep and deformation. Work is in progress on the investigation of the driving force and the kinetics of stress induced cavity growth at the grain boundary.

INTRODUCTION

The research undertaken in this program is a part of the continued effort of this laboratory to develop concepts and methods for the characterization of mechanical properties of crystalline solids. An important objective of this work is to generate information of interest to mechanical testing and mechanical design at elevated temperatures.

The approach adopted in this work is based on the concept of a mechanical equation of state proposed by Hart.¹ During the past year significant progress was made in its development. For the first time a complete model for non-elastic deformation in the grain matrix was established and tested by experimental data. Much of the work on the mechanical equation of state during this period was devoted to data analysis for the purpose of verifying this model. The comparison of the data of anelasticity tests and those of load relaxation experiments contributed also to the same purpose. It is believed that the availability of this model will enhance considerably the future work, for example in the investigation of the structure-property relationships and in the application of a mechanical equation of state in mechanical design.

During the last year Dr. E. W. Hart and the principal investigator were invited to present a keynote address on in-reactor creep and deformation in the 3rd International Conference on Zirconium in the Nuclear Industry. A paper entitled "The Use of State Variables in the Description of Irradiation Creep and Deformation of Metals" was prepared for this conference.

The experimental work on grain boundary gas bubbles, grain boundary cavities and intergranular fracture was progressing satisfactorily. Capabilities were developed during the past fiscal year to measure the growth of grain boundary cavities under applied stress as a function of grain boundary orientation and time.

An important objective of this project is to investigate the effect of grain boundary sliding on the stress induced growth of grain boundary cavities.

Continued effort was made during the past year to promote the application of the findings of the present program, especially the approach of a mechanical equation of state. In addition to the collaboration with the mechanics group at Cornell on mechanical design under the ERDA sponsorship, a new joint program under EPRI sponsorship on Type 304 stainless steel was initiated with the same mechanics group at Cornell and a mechanics group at G.E. Research and Development Center. The work on zircaloy with Westinghouse R&D center is progressing satisfactorily and will be continued. The principal investigator interacted also with the personnel of Argonne National Laboratory, Hanford Engineering and Development Laboratory, Combustion Engineering and other organizations on the approach of a mechanical equation of state.

In the following the progress of the past year will be described separately under (1) Mechanical Equation of State, (2) In-reactor Creep and Deformation and (3) Grain Boundary Gas Bubbles, Grain Boundary Cavities and Intergranular Fracture.

MECHANICAL EQUATION OF STATE

The work performed during the past year in this area emphasized the analysis of the data of load relaxation and load change (anelasticity) experiments for the purpose of verifying the new deformation model for grain matrix processes proposed by Hart¹. This deformation model will be introduced first prior to the discussion of the results of data analysis.

The Deformation Model

The deformation model is described in considerable detail and in three-dimensional context in reference (1). The description given here will be limited to uniaxial deformation for simplicity.

The theory² that underlies the model is phenomenological and thus leads

directly to deformation constitutive relations. The theory is a state variable theory, and the constitutive equations represent a plastic equation of state.

The model represents a synthesis of three deformation mechanisms in the grain matrix whose mutual relationship is most easily described by the rheological diagram of Fig. 1. The three mechanisms are represented by three elements labeled 1, 2, and 3. In the following discussion they will be referred by the names a-element (or stored strain element), α -element, and $\dot{\epsilon}$ -element (or frictional element) respectively. These elements and their relationships can be taken to represent familiar micro-mechanical processes as was discussed in reference (1). The micro-mechanical relationships are considered to be as follows:

The dislocation flux that is responsible for the non-elastic deformation of the metal grain matrix must traverse not only large regions of relatively well ordered crystal but also the strong barriers to dislocation motion due to dislocation tangles and cell walls. The strong barriers represent the basic strain hardening and are generated by straining. Dislocation motion in the good regions is limited by glide friction. Passage through the strong barriers can occur either by mechanical cutting of dislocations at high enough stress or by thermal activation at lower stresses. Since the dislocation flux in the good regions will generally exceed the rate of passage of barriers, there will be an accumulation of dislocations in pile-ups at the barriers. The pile-ups will generally raise the driving force for barrier passage and will generate back stresses that slow down the dislocation flux through good crystal.

In the model the α -element represents the barrier processes, the a-element characterizes the pile-ups as a stored strain, and the $\dot{\epsilon}$ -element represents the glide friction. The resultant mechanical interactions among the processes and the dislocation flux balance is then accounted for by the diagram of Fig. 1. These relations will now be described quantitatively.

The applied uniaxial stress σ is the sum of the stresses σ_a and σ_f that are operative in each branch of the diagram. The observed total inelastic uniaxial strain rate $\dot{\epsilon}$ is the same as the strain rate exhibited by the lower branch and is equal to the sum of the strain rate component $\dot{\alpha}$ and the time rate of change of stored strain a . Thus we have two constraint equations on the auxiliary variables σ_a , σ_f , $\dot{\alpha}$, and a . These are

$$\sigma = \sigma_a + \sigma_f, \quad (1)$$

$$\dot{\epsilon} = \dot{\alpha} + da/dt. \quad (2)$$

The constitutive equations for the component elements are as follows:

The a -element is a linear elastic element with a modulus M such that

$$\sigma_a = Ma. \quad (3)$$

The $\dot{\alpha}$ -element is the plastic-creep element satisfying the relations

$$\ln(\sigma^*/\sigma_a) = (\dot{\epsilon}^*/\dot{\alpha})^\lambda, \quad (4)$$

$$\dot{\epsilon}^* \equiv (\sigma^*/G)^m f e^{-(Q/RT)}, \quad (5)$$

$$d \ln \sigma^*/dt = \Gamma(\sigma_a, \sigma^*) \dot{\alpha} - R(\sigma^*, T). \quad (6)$$

In these equations T is the absolute temperature, R is the gas constant, G is the modulus of rigidity at temperature T , and λ , f , m , and Q are constants for each material. The functions Γ and R are to be determined experimentally.

The $\dot{\alpha}$ -element depends prominently on the scalar state variable σ^* which we shall call the hardness. The strain hardening is then conveniently represented by an evolution equation that provides for incremental increase of hardness with strain increments $d\alpha$ and for purely thermal recovery of hardness. In the work reported here, the recovery term R is entirely negligible. The structure of Γ is described in greater detail elsewhere^(1,3).

The $\dot{\epsilon}$ -element, which represents dislocation glide friction, can be represented over fairly large ranges of strain rate $\dot{\epsilon}$ as a non-linear viscous element with a power law behavior. In order to emphasize that $\dot{\epsilon}$ has the same

sign as σ_f we write this relation with the signum function (sgn) whose value is simply the algebraic sign of the argument. Thus

$$\dot{\epsilon} = \dot{a}^*(T) (|\sigma_f|/M)^M \text{sgn}(\sigma_f) . \quad (7)$$

We shall omit the signum and absolute value sign when both $\dot{\epsilon}$ and σ_f are positive. The rate variable $\dot{a}^*$ is to be measured as a function of temperature. The exponent M is a constant for any one material.

Some typical values of the material constants are: $M \approx 7-9$, $m \approx 4-5$, $\lambda = 0.15$, M is of the order of G , and Q is commonly the same as the activation energy for self-diffusion of the atomic species. It should be noted that the value of these constants does vary significantly from one material to another.

If a specimen, for which the initial value of a is zero, is loaded at an applied stress σ , the strain rate $\dot{\epsilon}$ is initially high, and it rapidly decreases to a lower more steady value. There then ensues a further much slower time rate of decrease of $\dot{\epsilon}$. The initial loading transient corresponds to a rapid increase in the value of a until the time when da/dt falls to a level much lower than $\dot{\epsilon}$. The subsequent slower rate of reduction of $\dot{\epsilon}$ is due principally to the continued strain hardening of the α -element. Now, in the transient-free stage, $\dot{a}$ is closely equal to $\dot{\epsilon}$ and so we can plot both σ_a and σ_f against $\dot{\epsilon}$. This is done schematically in Fig. 2 for a fixed value of σ^* , and for a typically low homologous temperature case. The curve of operative applied stress σ is shown as the sum of σ_a and σ_f , and in such a temperature range it is typically concave upward as a function of $\dot{\epsilon}$. The σ_a curve as shown becomes asymptotically tangent to the line $\sigma = \sigma^*$ at large $\dot{\epsilon}$ and so at sufficiently low temperature σ^* appears substantially as a plastic yield stress for the α -element. This is in fact the situation for the 316 Stainless Steel of the current experiment.

A considerably simplified version of the mechanical equation of state for the transient free behavior at low homologous temperatures can be formulated as follows:

$$da/dt \neq 0, \quad (8)$$

and so

$$\dot{\alpha} = \dot{\epsilon} . \quad (9)$$

Now to a very good approximation

$$\sigma_a = \sigma^* , \quad (10)$$

and so

$$\sigma_F = \sigma - \sigma^* . \quad (11)$$

Then $\dot{\epsilon}$ can be obtained directly from Equation (7) as

$$\dot{\epsilon} = \dot{\alpha}^* [(\sigma - \sigma^*)/M]^M . \quad (12)$$

This equation can be rewritten in the form

$$\dot{\epsilon} = \dot{\alpha}^* (\sigma^*/M)^M [(\sigma/\sigma^*) - 1]^M . \quad (13)$$

Then, if σ is scaled by σ^* , and $\dot{\epsilon}$ by $(\sigma^*/M)^M$, the resultant scaled $\dot{\epsilon}$ vs σ curve is a single invariant curve. This means that a set of transient-free $\ln \dot{\epsilon}$ vs $\ln \sigma$ curves at a variety of values of σ^* can be made to superpose exactly by translation along a fixed direction with slope $1/M$ at low homologous temperatures. Such a behavior has been reported by Yamada and Li for Type 316 austenitic stainless steel.⁴

The important thing about the scaling behavior is that it provides an experimental determination of the exponent M from the scaling direction independently of the shape of the curves.

The same theory that describes the transient-free behavior also makes a unique prediction of the transient behavior. The transient, at low homologous temperature, is most sensitively measured at low stresses since the relaxation time for the transient is then much longer than at a high stress level. Furthermore, if σ is much smaller than σ^* , $\dot{\alpha}$ is entirely negligible and the $\dot{\alpha}$ -element is effectively frozen. The model then appears simply as an anelastic body with Hookean spring but with non-Newtonian dash-pot. In this range $\dot{\alpha}=0$ and

$$\dot{\epsilon} = da/dt . \quad (14)$$

The resultant constitutive equation for this behavior (writing $\dot{a}$ for da/dt) is

$$\dot{a} = \dot{a}^* [(\sigma - \sigma_a)/M]^M. \quad (15)$$

Now application of Equation (3) leads to the equation

$$\dot{a} = \dot{a}^* [(\sigma/M) - a]^M, \quad (16)$$

or if we introduce the saturation anelastic strain a^s for σ/M this can be written

$$\dot{a} = \dot{a}^* [a^s - a]^M. \quad (17)$$

It can be deduced from a single model therefore the behavior of the deformation at low homologous temperature both in the fully plastic range for which $\sigma > \sigma^*$ and in the anelastic range for which $\sigma < \sigma^*$. The predictions for the former case are given simply by Equations (12) and (13) and in the latter case by Equations (16) and (17). Tests of either case will completely determine the material constants M and $\dot{a}^*$ if M is known, and M is determined by the anelasticity tests. A crucial test of consistency, then, is the extent of agreement of the values of M and $\dot{a}^*$ determined by the two types of measurement.

Tests are reported in the following for both high and low σ behavior for 316 Stainless Steel. The consistency of the predictions will be shown to be quite good.

The transient-free behavior at high homologous temperatures is described graphically in Fig. 3. As in Fig. 2 three curves are also shown. The lowest curve, that is displayed only in a finite observable strain rate interval, represents the $\dot{\epsilon}$ -element of Fig. 1 and of Eq. 7. The next higher curve is the $\dot{\sigma}$ -element of Fig. 1 and obeys Eqs. 4 and 5. Because of Eq. 5, a different segment of the $\dot{\sigma}$ -element curve appears due to the difference in temperature, in the fixed observable strain rate interval in Fig. 3 compared to that in Fig. 2. The parameter σ^* is assumed to be large compared to the stress level of the $\dot{\epsilon}$ -element curve. The highest curve is the locus of points that represent, at each value of $\dot{\epsilon}$, the sum of the stresses of the two lower curves in accordance with Eq. 1. That curve is the observable σ - $\dot{\epsilon}$ curve at the given value of σ^* .

It is shown to be concave downward represents the typical load relaxation data obtained at high homologous temperatures and represents essentially the behavior of the $\dot{\alpha}$ -element (Equations 4 and 5).

An important feature of the curves of high homologous temperatures is that they could also be generated by scaling of stress and strain well demonstrated by the load relaxation data.⁵ The parameter μ , the slope of the scaling direction, is the reciprocal of the parameter m in Eq. 5. This scaling with respect to σ^* is described analytically by Eqs. 4 and 5. It should be noted that the slope of the scaling direction at high homologous temperatures is different from that at low homologous temperatures.

The transient-free behavior at intermediate temperatures is governed both by the $\dot{\alpha}$ -element and the $\dot{\epsilon}$ -element. Analytically it is described by Equation (1) with the σ_a and σ_f given by Equations 4 and 7 respectively. In this temperature region the simple scaling relationships described previously will no longer be applicable and the constant hardness $\log \sigma - \log \dot{\epsilon}$ curves obtained in load relaxation experiments will show an inflection point. Since the $\dot{\epsilon}$ -element is relatively temperature insensitive the present deformation model will predict a marked reduction of the apparent activation energy at lower temperatures.

In the following section the results of the data analysis will be described to support the validity of the deformation model.

Comparison with Experimental Data

Much of the work during the past year was devoted to the analysis of the existing data for the purpose of verifying the deformation model described in the previous section. Additional data were obtained as required for the same purpose. Two types of data were used in the data analysis. The first type consisted of load relaxation data in the form of constant hardness $\log \sigma - \log \dot{\epsilon}$ curves covering a wide range of test conditions and deformation variables. They were used to show the general applicability of the deformation model. The second type consisted of

load change (anelasticity) data obtained at low homologous temperatures and low stresses and also load relaxation data in the same temperature region but at high stresses. These data were used to demonstrate that the $\dot{\epsilon}$ -element (frictional) in the deformation model represented both types of data well, therefore provided a severe consistency test. In the following the two types of data will be discussed separately.

1) Load Relaxation Data:

The data of interest included those of Type 316 austenitic stainless steel, nickel and zircaloy-4.

The typical constant hardness $\log \sigma - \log \dot{\epsilon}$ data at various temperatures of Type 316 austenitic stainless steel are shown in Fig. 4.

Qualitatively the data in Figure 4 exhibits the behavior described in the previous section. At lower homologous temperatures the measured $\log \sigma - \log \dot{\epsilon}$ curves are concave upward. As the temperature increases, the contribution of the dislocation glide controlled component becomes less important. At intermediate temperatures the measured curves show an inflection point. At 500°C the measured curve becomes concave downward.

Equations 1, 4, 5 and 7 were used to fit the experimental data for the purpose of quantitatively testing the deformation model. An iterative numerical process was used to evaluate the parameters in these equations from the experimental data. The results of the calculations are given in Table 1. The solid curves in Figure 4 are calculated by using the parameters in Table 1 and are seen to represent the experimental data well.

The experimental data in Figure 4 cover a wide range of temperature, stress and plastic strain rate and includes $\log \sigma - \log \dot{\epsilon}$ curves of a variety of shapes. The possibility that they can be described by the single set of parameters given in Table 1 and Equations 1, 4, 5 and 7 indicates the general validity of the deformation model proposed by Hart.¹

The calculated values of $M\dot{\epsilon}^*^{-1/M}$ in Equation 7 is plotted as a function of temperature in Figure 5. It decreases with increasing temperature but does not show an exponential temperature dependence. Physically the quantity $M\dot{\epsilon}^*^{-1/M}$ represents the strength of the frictional resistance that can be affected by lattice vibration, solute content, etc. and is not strongly dependent on temperature.¹ The results in Figure 5 support the prediction of the deformation model.

The data in Figure 4 can be replotted in the form of constant hardness and stress, $\log \dot{\epsilon}$ vs. $1/T$ curves. The slope of these curves gives the apparent activation energy Q_{app} for plastic deformation. These curves show that the apparent activation energy depends both on temperature and stress. Quantitatively, this dependence can be found from the temperature dependence of the parameter $\dot{\epsilon}^*$ and $\partial \ln \dot{\epsilon}^* / \partial (1/RT) \big|_{\sigma, \sigma^*} = Q_{diff} / RT^2$ where Q_{diff} is the activation energy for diffusion and reported to be 65 kcal/mole.

In Figure 6 the calculated Q_{app} is plotted against temperature for two different stresses. At lower temperatures where dislocation glide is controlling, the Q_{app} reflect mainly the temperature dependence of the rate constant $\dot{\epsilon}^*$. At higher temperatures the Q_{app} approaches the activation energy for diffusion. In the intermediate temperature range the Q_{app} varies with temperature. Similar temperature dependence has been observed in creep measurements.

According to Equation 7, in the region where dislocation glide controlled process is important, the slope of the translation path for the constant hardness $\log \sigma - \log \dot{\epsilon}$ curves should be the inverse of the value of the exponent M . Experimentally the data in Figure 7 gives the slope of the translation path to be 0.13 ± 0.02 which is consistent with the value of M in Table 1 obtained from the data in Figure 2. This agreement also supports the deformation model.

Table I
Parameters for Type 316 Stainless Steel

Temp (°C)	σ^* (psi)	$\dot{\epsilon}^*$ (sec ⁻¹)	λ	$M\dot{a}^{*-1/M}$ (psi)	M
500	76,115	4.248×10^{-18}	.15	500	7.6
400	75,622	8.201×10^{-21}	.15	3,416	7.6
300	75,327	1.790×10^{-24}	.15	7,699	7.6
200	75,335	1.099×10^{-29}	.15	13,879	7.6
150	75,531	3.272×10^{-33}	.15	17,505	7.6
25	75,584	3.292×10^{-47}	.15	26,246	7.6

Similar load relaxation data of single crystal and polycrystal nickel were obtained in the form of constant hardness $\log \sigma - \log \dot{\epsilon}$ curves (for example, those shown in Figs. 8 and 9). The curves in these figures are not of the same hardness. It is seen from these figures that the experimental data are well represented by the deformation model and provide an additional support of its validity. The value of $M\dot{a}^{*-1/M}$ which measures the resistance to dislocation glide shows a maximum in the temperature range of the experiment (Fig. 10). This is a very interesting result and suggests the possibility of using the present approach as an effective means for the investigation of the solute-dislocation interactions. The work hardening properties of polycrystal nickel were also measured during the past year from the view point of the deformation model. The work hardening data as well as the results of the analysis of load relaxation data will not be described in detail here. The latter information is discussed in reference 6.

The work on zircaloy-4 is still in progress. Some of the typical load relaxation data in the form of constant hardness $\log \sigma - \log \dot{\epsilon}$ curves are shown

in Fig. 11. Even though a complete picture from the viewpoint of the present approach has not emerged from the work, the results of the preliminary data analysis has produced significant insight as to the mechanical behavior of this alloy system which are noted for its complexity. The solid lines in Fig. 11 are the calculated curves based on the deformation model which describes the grain matrix processes only. At higher temperatures the calculated curve is seen not to fit the experimental data. These results suggest the possibility of the contribution of grain boundary sliding. The temperature of 350°C is not usually considered to be a high temperature in the homologous temperature scale for zircaloy. One does not expect therefore that grain boundary sliding will be important in this homologous temperature range. The suggestion based on the present data, of the existence of grain boundary sliding can be important to the current problem of delineating the failure mechanisms of zircaloy cladding of the light water reactors.

The room temperature data of zircaloy shown in Fig. 11 cannot be represented by the deformation model if the same parameters as those for the higher temperature curves are used. Strain aging effects as well as temperature dependent anisotropy can be the cause of the observed discrepancy. Efforts are being made to pursue these possibilities in order to fully understand the deformation properties of zircaloy.

2) Load Change (Anelasticity) Data:

The load change and load relaxation data of Type 316 stainless steel and nickel obtained under conditions where the $\dot{\epsilon}$ -element (frictional) predominated were compared to show that they could be described by the same set of constants and thus provided a test of the consistency of the deformation model. In the following only the data of Type 316 stainless steel will be discussed. The anelasticity data were obtained in the work sponsored by NSF.

The load relaxation data used in the comparison are shown in Fig. 7. These curves can be superposed by translation along the line shown in the figure. The slope of that line, according to Equation 12 is $1/M$. The value of the exponent

obtained this way is 7.7 ± 0.2 . Since the range of hardness of the curves in Fig. 7 is small, the accuracy of determination of M is not very sharp by this means. A sharper determination of M is obtained by fitting the actual shape of the curves according to Equation 12. By that means M is found to be 7.8 ± 0.1 .

The solid lines through the data points in Fig. 7 are plots of Equation 12 with $M = 7.8$ and the parameter values shown in Table II. The value of M_m has been taken to be $1.01 \times 10^5 \text{ MN/m}^2$ as determined in the anelasticity analysis below and $\dot{a}^* = 1.65 \times 10^{21} \text{ sec}^{-1}$.

In the anelasticity test the strain is measured as a function of time after an abrupt stress change which can be either positive or negative. The typical anelastic strain vs time data are shown in Fig. 12. The non-linear relation of Equation 17 was found to provide a good fit for the observed data.

Integration of Equation 17 yields

$$(a_m^s - a_m^o)^{1-M} - (a_m^s - a_m)^{1-M} = (1-M)\dot{a}_m^*(t-t_o) \quad , \quad (18)$$

where a_m^o is the grain matrix anelastic strain at time $t = t_o$. This equation was used to analyze the grain matrix anelastic strain by means of a non-linear least squares fitting routine. The best fit curves to two of the test runs are shown plotted with the data points in Fig. 12.

The average values of the best parameters determined individually from four runs are: $M = 7.7 \pm 0.2$, $\dot{a}_m^* = 7.0 \pm 2.0 \times 10^{20} \text{ sec}^{-1}$, and $M_m = 1.46 \pm 0.07 \times 10^7 \text{ psi}$ ($1.01 \pm 0.05 \times 10^5 \text{ MN/m}^2$). The separate individual determinations are listed in Table III.

More pertinent for the current experiment is the value of $\dot{a}_m^*$ obtained with a single value of M for all runs. These are also shown in Table III for the single "best" value $M = 7.8$. For that case the geometric mean value of $\dot{a}_m^*$ is $1.14 \times 10^{21} \text{ sec}^{-1}$. This value is uncertain to within a factor of about 2.5.

The principal feature of the model that was under test was the $\dot{\epsilon}$ -element.

This non-linear frictional term is characterized by the rate constant $\dot{a}_m^*$ and a stress exponent M . Both ranges of data were fit quite well over a broad range of strain rate with $m = 7.8$. The best values of $\dot{a}_m^*$ were $1.65 \times 10^{21} \text{ sec}^{-1}$ for the high stress data and 1.14×10^{21} for the low stress data. These agree quite well within the experimental uncertainty.

Table II

The Constants in Equation 12 for Curves in Figure 7

Curve	$\epsilon\%$	$\sigma^*(\text{psi})$	$(\dot{a}_m^*/M_m^M)^{-1/M}$	M
1	20.75	92967	26500	7.6
2	21.49	93807	28000	7.6
3	22.69	95378	30500	7.6

Table III

Experimental Data and Values of the
Calculated Grain Matrix Anelastic Parameters

σ Initial Stress MN/m^2	$\Delta\sigma$ MN/m^2	Δa_m^s	M_m MN/m^2	$\dot{a}_m^*$ sec^{-1}	M	$\dot{a}_m^*$ for $M=7.8$ sec^{-1}
8.78	34.58	35.5×10^{-5}	0.97×10^5	5.4×10^{20}	7.86	3.7×10^{20}
43.36	-34.54	33.5×10^{-5}	1.03×10^5	9.68×10^{20}	7.69	1.9×10^{21}
21.08	17.32	18.0×10^{-5}	0.96×10^5	5.1×10^{20}	7.80	5.1×10^{20}
38.4	-17.24	16.0×10^{-5}	1.07×10^5	7.4×10^{20}	7.51	4.7×10^{21}

In summary, based on the data analysis presented in this section it can be concluded that the deformation model based on a mechanical equation of state is found to be supported by the experimental data. In the future work the validity of the deformation model will be tested further and emphasis will be made also in its various applications, for example, in the basic understanding

of mechanical properties and in mechanical testing and design.

IN-REACTOR CREEP AND DEFORMATION

During the past year attempts were made to apply the deformation model to the description of in-reactor creep and deformation. It was shown that this model represents the existing in-reactor creep data as well as various current micro-mechanical models. The available data are of a very limited range to be sufficient to delineate the applicability of these different approaches. The present deformation model suggests however the possibility of performing a combination post-irradiation load relaxation experiments and load relaxation experiments under ion-bombardment to obtain the required data to test its applicability. The suggested experiments are less costly compared to the current in-reactor tests and if proven to be applicable, can be used also as a practical tool for collecting design data.

The present approach proposes that considerably greater use can be made of thermal environment test data, for both irradiated and unirradiated material, in order to characterize the behavior under irradiation. Since considerably more data can be collected over broader ranges of test variables out-of-reactor, it is clear that any success of such utilization would be highly advantageous.

Irradiated material is a relatively strong material. For such materials σ^* can be expected to be rather high because of second phase hardening and possibly because of deliberate high strain hardening levels. Under those circumstances σ_f is small compared to σ_a and thus the operative flow stress σ is determined almost entirely by σ_a . The $\dot{\alpha}$ -element is considered as the flow controlling mechanism, and the constitutive equations can be simplified as

$$\ln(\sigma^*/\sigma) = (\dot{\epsilon}^*/\dot{\epsilon})^\lambda, \quad (19)$$

$$d \ln \sigma^* / d \dot{\epsilon} = \Gamma(\sigma, \sigma^*), \quad (20)$$

where the recovery term R is ignored, and Eqn. 5 stands as before.

This form of the deformation model will be used to discuss the proposed

extension to radiation environment behavior. The principal features of this model are the explicit analytical form of the stress-strain rate relationship (Eqn. 19) and the dependence on the state variable σ^* . The auxiliary variable $\dot{\epsilon}^*$ is dependent on σ^* and T in the thermal environment case and is given by Eqn. 5. These relationships will be altered by the effects of radiation.

It is proposed that the stress dependence of the strain rate under radiation conditions can also be represented by Eqn. 19 and that the appropriate values of σ^* and $\dot{\epsilon}^*$ can be determined as a function of fluence and current flux. These two functional dependences will be considered separately.

1) The Fluence Effect:

The fluence experienced by a specimen results in a modification of the micro-structure of the material. If an irradiated specimen is tested out-of-reactor, it should behave like a material with altered micro-structure in much the same way as if such alteration had occurred by some other metallurgical processing or aging. This results merely in a change of σ^* and $\dot{\epsilon}^*$.

The important point here is that the form of the σ - $\dot{\epsilon}$ curve is insensitive to the details of micro-structure. Even the value of λ is unchanged. The effect of micro-structural change is expressed entirely in terms of displacement of the point $(\sigma^*, \dot{\epsilon}^*)$ in the σ - $\dot{\epsilon}$ space. It is anticipated that there will also be a fluence effect on the friction constant k^* in the complete model.

2) The Flux Effect:

The most direct effect of radiation flux is to establish a supersaturation of point defects over the thermal equilibrium concentration. Such supersaturation can increase the rate of those processes that depend on dislocation climb. In his review article Nichols⁷ discusses several of the proposals concerning the effect on radiation creep. He considers both those mechanisms that depend on a bias in the defect absorption at dislocations and those that are independent of such bias. In the present treatment attempts will not be made to establish

a detailed micro-mechanical model. It is assumed however, that the strain results from glide, and that the strong barriers or obstacles are passed by diffusive processes. The effect of radiation flux is to cause a positive displacement of $\ln \dot{\epsilon}^*$ in the same way as might be brought about by effective temperature increase. This effective temperature increase can be estimated, but it is proposed that it be measured as a function of flux and energy. A flux effect on $\dot{\epsilon}^*$ is also expected. The effect is probably to increase $\dot{\epsilon}^*$, i.e., to reduce the dislocation friction.

The Proposed Representation and Application:

The combined effects of flux and fluence in the non-transient creep range are expected to be represented entirely in terms of the pair of state variables σ^* and $\dot{\epsilon}^*$. These two variables can be considered conveniently as the point $(\ln \sigma^*, \ln \dot{\epsilon}^*)$ in a plot of $\ln \sigma$ vs. $\ln \dot{\epsilon}$. Such a plot is shown at a single temperature in Fig. 13. The three labeled points show schematically the effects discussed above. The point labeled 1 represents the state point for unirradiated material at some level of hardness according to prior strain history. The solid line through that point is the focus of state points at other levels of hardness. Point 2 represents the state point for irradiated material, but for deformation behavior in thermal environment. The shift from 2 to 3 represents the displacement to higher $\dot{\epsilon}^*$ value due to radiation flux level. For each of these cases the expected experimental stress-strain rate relationship is given by Eqn. 19 with the values of σ^* and $\dot{\epsilon}^*$ determined by the appropriate state point.

Now what remains to be determined is the dependence of the state point displacements on the radiation fluence and flux. That relationship must be determined experimentally.

1) 304 Stainless Steel:

Post-irradiation load relaxation tests have been made at Argonne National Laboratory by Yamada⁸ on 304 Stainless Steel following an exposure of 1.82×10^{22}

neutrons/cm² of energy greater than 0.1 MeV. Those measurements at 25°C and 300°C confirmed that the $\dot{\epsilon}$ -element curve was of the same shape as for the un-irradiated material and determination of post-irradiation values of σ^* and $\dot{\epsilon}^*$ were made. On the basis of that testing it is possible to predict a thermal σ - $\dot{\epsilon}$ curve at 400°C using a value of Q of 65 Kcal/mol in Eqn. 5. That curve is shown in Fig. 14 together with a curve displaced in strain rate to what would correspond to thermal behavior at 700°C. The calculations of Harkness and Li⁹ concerning void formation can be used to show that this is a reasonable effective temperature shift at this dose level for the flux conditions characteristic of the creep rate measurements of Slimm *et al*¹⁰. Those creep rate results are plotted on the displaced curve in Fig. 14.

The consistency of the representation is encouraging. However, the plot in Fig. 14 implies some conflict with the claim of Newtonian behavior of ref. 10. The present plot would imply a stress exponent closer to three. Clearly, the experimental range of the data is not sufficient to settle this question.

2) Zirconium Alloys:

Post-irradiation values of σ^* for zircaloy can be estimated from post-irradiation tensile test data, but no measurement of $\dot{\epsilon}^*$ is possible because of the absence of load relaxation data.

In Fig. 15 plots of the data from two of the radiation creep test available in the literature are shown, those by Ibrahim¹¹ and by Gilbert and Mastel¹². The solid curve is from Eqn. 8 with $\lambda = 0.15$ and $\log \sigma^* = 5.2$. It is seen that Eqn. 19 gives a good representation of the experimental data.

In summary, the results presented in this section represent a first attempt of the application the deformation model to the description of the in-reactor creep and deformation. It demonstrated clearly the inadequacy of the existing data. The principal investigator feels that load relaxation testing, both in-and-out-of reactor, is the most efficient way of making the crucial tests and should be given some consideration in the existing ERDA programs.

GRAIN BOUNDARY GAS BUBBLES, GRAIN BOUNDARY CAVITY
AND INTERGRANULAR FRACTURE

Experimental efforts were made during the past year to develop capabilities which will allow the investigation of the driving force and the kinetics of stress induced cavity growth at the grain boundary. These efforts included the production of stable methane bubbles, the measurement of grain boundary orientation relative to the applied stress axis in the SEM and the measurement of cavity size in the SEM. In the following some preliminary experimental results of nickel will be shown to demonstrate that the required experimental capabilities are well developed for this project.

Grain boundary cavity can be nucleated during deformation due to the incompatibility between grain boundary sliding and grain matrix deformation. This is apparently an easy process based on experimental observations. It can be nucleated also in the form of gas bubbles in the absence of deformation by collecting helium atoms or by the formation of methane at the grain boundary.

Once the grain boundary cavity is formed, under applied stress it will grow. Stress induced atomic transport is an important process by which the grain boundary cavity can grow. This is exactly analogous to diffusional creep suggested by Herring where the driving force is the normal stress at the grain boundary and the grain boundary serve as the source of vacancies and the cavity as the sink.

Atomic transport controlled grain boundary cavity growth has been investigated extensively both theoretically and experimentally in the past. The kinetics of cavity growth were usually measured on specimens from a creep experiment in the past during which the nucleation and the growth of the grain boundary cavities occurred simultaneously. In the present work the initial grain boundary cavities are produced in the absence of applied stress in the form of stabilized methane bubbles. Therefore the growth kinetics can be investigated under applied stress without the interference of the nucleation processes.

The driving force for the growth of grain boundary cavities is the component

of the applied stress normal to the boundary plane. The possibility exists that the grain boundary normal stress can be reduced or relaxed depending on the extent of grain boundary sliding. This possibility is consistent with experimental observation in that cavity growth has been found to occur predominately on the grain boundary which is normal to the applied stress where grain boundary sliding is absent. In life time predictions, the influence of grain boundary sliding can therefore play an important indirect role.

In the present work the growth rate of grain boundary cavities will be measured as a function of grain boundary orientation relative to the applied stress axis. This is a laborious task and much of the work during the past year was devoted to the development of the capabilities for this measurement.

The initial grain boundary cavities were produced by exposing the nickel specimen to high pressure hydrogen at elevated temperatures followed by annealing in the absence of hydrogen also at elevated temperatures to stabilize the size of the cavities.

The latter step is necessary because the condition of the methane reaction of the present work is such that the growth of the cavity during hydrogenation was found to be limited by the rate of vacancy absorption. Therefore the internal pressure of the methane gas at the end of hydrogenation was greater than $2\gamma/r$ where γ is the surface tension and r is the radius. During annealing after hydrogenation the cavity will therefore grow by absorbing more vacancies till the methane pressure is balanced by $2\gamma/r$. The existence of high methane pressure after hydrogenation can be important also in the fracture behavior of hydrogenated materials at low temperatures.

Fig. 16 shows the typical grain boundary surface obtained by fracturing the specimen at the liquid nitrogen temperature. Fig. 17 shows a higher magnification of a similar grain boundary surface where the cavities are more clearly illustrated.

The capability of measuring the kinetics of cavity growth can be demonstrated by the data shown in Fig. 18. These data show the growth of the grain boundary

cavities after hydrogenation at 600°C in the absence of applied stress. The driving force for cavity growth here was the internal methane pressure. The hydrogenation was carried out at 500°C and a hydrogen pressure of 2500 psi and an exposure time of three hours. The slope of the average $\log(a^2 - a_0^2)$ vs log time plot is 0.35 ± 0.05 where a is the cross sectional area of the cavity as revealed by the SEM. The measured value of the slope is consistent with the predicted value based on the vacancy absorption model and demonstrates the accuracy of the kinetic measurement.

In another sequence of the experiment, nickel specimens which were given the same hydrogenation treatment as described above and annealing in the absence of hydrogen for six days at 600°C were stressed under an uniaxial tension of 3930 psi and at 500°C for 143 hours. The initial size distribution of the grain boundary cavities as well as those as a function of grain boundary orientation after stressing are given in Fig. 19. The grain boundary angle is measured such that an angle of zero degree corresponds to a grain boundary normal to the applied stress axis. It is seen from these data that the rate of growth is higher for the grain boundary which is closer to the normal of the applied stress. For the level of the applied stress of the experiment, the contribution of grain boundary sliding is not important. The grain boundary normal stress should vary therefore with the grain boundary orientation simply as a function of $\cos^2\theta$ based on the geometrical decomposition. Since the growth kinetics is such that the cavity radius is proportional to time with an exponent of 0.4, the average of $a^{1.25}$ is plotted as a function of grain boundary orientation in Fig. 20. The solid line in Fig. 20 is a calculated curve with $\cos^2\theta$ dependence. It is seen from this figure that the ability of measuring the orientational dependence is satisfactory.

This project is presently in progress with the objectives 1) to measure the kinetics of stress induced cavity growth and 2) to evaluate the influence of grain boundary sliding in reducing the normal stress at the grain boundary.

SUMMARY

1) The deformation model based on mechanical equation of state was found to be able to account for the load relaxation and anelasticity data of Type 316 austenitic stainless steel and nickel.

2) The same model was applied to describe in-reactor creep and deformation with some success.

3) Experimental capabilities were developed for the investigation of the driving force and the kinetics of stress induced cavity growth at the grain boundary.

REFERENCES

1. E. W. Hart, Trans. A.S.M.E., Journal of Engineering Materials and Technology, 1976, in press.
2. E. W. Hart, Acta Metallurgica, Vol. 18, 1970, pp. 599.
3. G. L. Wire, F. V. Ellis and Che-Yu Li, Acta Metallurgica, Vol. 24, 1976, pp. 677.
4. H. Yamada and Che-Yu Li, Met. Trans., 22, 1974, pp. 249.
5. E. W. Hart, C. Y. Li, H. Yamada, and G. L. Wire, in Constitutive Equations in Plasticity, A. S. Argon, ed., M.I.T. Press, Cambridge, MA, 1975, pp. 149.
6. S. J. Chao, "Plastic Equation of State in Nickel", M.S. Thesis, Cornell University, Dept. of Materials Science and Engineering, 1976.
7. F. A. Nichols, "Radiation-Enhanced Creep", ERDA Research and Development Report WAPD-T-2636, Bettis Atomic Power Lab., West Mifflin, PA, Oct. 1975.
8. H. Yamada, unpublished data.
9. S. D. Harkness and Che-Yu Li, Metallurgical Transactions, Vol. 2, 1971, pp. 1457-1470.
10. J. Slimm, G. L. McVay, and L. C. Walters, "In-Reactor Deformation of Solution Annealed Type 304L Stainless Steel", in Proceedings of International Colloquium on the Measurement of Irradiation Enhanced Creep in Nuclear Materials, May 5, 1976, EURATOM, Petten, Netherlands, to be published.
11. E. F. Ibrahim, "In-Reactor Creep of Zr-2.5 Nb Tubes at 570°K", Zirconium in Nuclear Applications, A.S.T.M. STP 551, American Society for Testing and Materials, 1974, pp. 249-262.
12. E. R. Gilbert and B. Mastel, Transactions, American Nuclear Society, Vol. 12, 1969, p. 132.

FIGURE CAPTIONS

- Fig. 1 A diagram representing the mechanical and kinematical relationships among the deformation mechanisms for inelastic behavior of metals. Element 1 is Hookean; element 2 is the $\dot{\alpha}$ -element; element 3 is a non-linear viscous element.
- Fig. 2 A graph of stress vs. strain rate for transient free flow at low temperature. The observed flow stress σ , as shown by the upper curve, is the sum of the stresses represented by the two lower curves.
- Fig. 3 A graph of stress vs. strain rate for transient free behavior at high temperature. The applied stress σ is the sum of σ_a and σ_f . When σ_f is small, σ is nearly the same as σ_a . The hardness σ^* is an asymptote for the σ_a curve at large $\dot{\epsilon}$.
- Fig. 4 Constant hardness $\log_{10} \sigma$ vs. $\log_{10} \dot{\epsilon}$ data for Type 316 stainless steel at several temperatures. Stress values are modulus corrected for temperature. The stress scale shown is that for room temperature.
- Fig. 5 The quantity $(\frac{\dot{\alpha}^*}{M_0 M})^{-\frac{1}{M}}$ for Type 316 stainless steel for the glide controlled component in Equation 2 vs. Temperature, showing non-exponential temperature dependence.
- Fig. 6 Calculated apparent activation energies for plastic deformation vs. temperature plots for two different stresses for Type 316 stainless steel.
- Fig. 7 $\log_{10} \sigma$ vs. $\log_{10} \dot{\epsilon}$ data of Type 316 stainless steel obtained from room temperature load relaxation experiments at several plastic strain levels. The curves are calculated by using Equations 2, with the parameters in Table II.
- Fig. 8 $\log_{10} \sigma$ vs. $\log_{10} \dot{\epsilon}$ data for poly-crystal nickel at several temperatures. The curves are calculated by using Equations 1 and 4.
- Fig. 9 $\log_{10} \sigma$ vs. $\log_{10} \dot{\epsilon}$ data for single crystal nickel at 400°C and 500°C.
- Fig. 10 The quantity $(\frac{\dot{\alpha}^*}{M_0 M})^{-\frac{1}{M}}$ for nickel for the glide controlled component vs. Temperature.

- Fig. 11 $\log_{10}\sigma$ vs. $\log_{10}\dot{\epsilon}$ data for Zircaloy-4 at several temperatures.
- Fig. 12 Loading and unloading experimental data of grain matrix anelastic strain as a function of time after stress change for Type 316 stainless steel. The uncertainty in the strain is of the order of 3×10^{-6} .
- Fig. 13 Points representing several values of the state variable pair (σ^* , $\dot{\epsilon}^*$). Point 1 is for unirradiated material; point 2 is a result of fluence for out-of-reactor behavior; point 3 includes the shift of strain rate due to flux. Point 1 simply displaces along the solid line with increased straining.
- Fig. 14 Radiation creep rates, according to Slimm et al [8], plotted on a constant hardness curve for 304 stainless steel.
- Fig. 15 Radiation creep rates of 2x-2.5 Nb plotted on a constant hardness curve with $\lambda = 0.15$, $\log \sigma^* = 5.2$. The data points are from Ibrahim¹² (2% cold worked) and Gilbert and Mastel¹³.
- Fig. 16 Scanning electron micrograph of transgranular and intergranular fracture of nickel.
- Fig. 17 Scanning electron micrograph of the hydrogen induced bubble distribution in nickel.
- Fig. 18 The growth of grain boundary cavities induced by hydrogenation in nickel at 600°C without applied stress.
- Fig. 19 The size distribution of grain boundary cavities vs. grain boundary orientation under the influence of stress in nickel.
- Fig. 20 Cavity size as a function of grain boundary orientation in nickel.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

GRAIN MATRIX ANELASTIC STRAIN α_m
(ARBITRARY ZERO)

Figure 12

Figure 13

Figure 14

Figure 15

Scanning electron micrograph of
transgranular fracture of nickel.
(500X)

Scanning electron micrograph of
intergranular fracture of nickel.
(500X)

Scanning electron micrograph of
the hydrogen induced bubble distribution
used in this experiment.
(5000 X)

Scanning electron micrograph of
overcharged nickel specimen showing
extensive bubble formation and growth.
(2000X)

Figure 18

Figure 19

Figure 20