THE INFLUENCE OF PRECURSOR STRUCTURE ON THE DEVELOPMENT OF POROSITY IN POLYMER-DERIVED SiC

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ABSTRACT

Polymer-based routes to ceramic oxides take advantage of precursor chemistry and structure to produce materials with a range of pore sizes. Polymer precursor routes to non-oxide ceramics offer products with superior thermal and chemical stability in many cases. Polymethylsilane (PMS), a versatile cross linked SiC precursor, $[(\text{MeHSi})_x(\text{MeSi})_y]$, was synthesized using published procedures to yield fluid precursors with a low (20-40%) degree of cross linking. Unique, highly cross linked (60-70%), solid polymers were produced under reaction conditions which carefully conserve the volatile monomer. These two polymers were converted to SiC to determine the relative importance of the various contributions to porosity, and to assess the role of precursor structure on porosity development in non-oxides. Initial results indicate that precursor structure has little effect on porosity. The development of the porosity appears to be dominated by high temperature thermochemistry and/or microstructural changes.

INTRODUCTION

Porous SiC is desirable for gas separations, filters, catalysis, sensors, and a number of other applications. Within the last 15 years a large number of inorganic polymer precursors to SiC and other non-oxide ceramics have been developed [1,2]. These precursors provide relatively low temperature routes to non-oxides, facilitate the formation of objects with complex geometries, and make thin film production via low capital cost methods such as dip- and spin-coating possible. Ceramics formed from pre-ceramic polymers generally do not approach the densities of pure, crystalline forms of non-oxides and retain some porosity [3,4]. This porosity is undesirable in customary high temperature structural applications, thus limited research has been done to investigate the development of porosity from precursors and to exploit it in various applications.

Precursor routes to non-oxides generally involve the synthesis of polymers or oligomers containing the elements of the desired ceramic product (Si, C, N, B, etc.), conversion of the polymer into an amorphous covalent ceramic via pyrolysis in an inert atmosphere (at 700-1000°C), and if desired, transformation of the material into its crystalline components (at >1200°C). Most previous efforts to produce porous non-oxides from precursors involved very high [5] ($\geq 1400^\circ\text{C}$) or relatively low [6] ($\leq 550^\circ\text{C}$) processing temperatures. The high temperature routes require time and energy intensive processing steps and any substrate used with these non-oxides must be stable to at least 1400°C. The low temperature materials may retain organic sites that limit their thermal and chemical stability. However some studies [3,4,7] report the development of significant amounts of porosity from 700-1100°C. Studies of Si-C-N-O fibers showed pore volumes of 5 and 25% and pore diameters of 10 and 20 Å [4]. Polymer derived BN powders showed high surface areas ($\sim 700 \text{ m}^2/\text{g}$) with a high percentage of microporosity. The precursor reaction chemistry, precursor polymer structure and pyrolysis conditions all influence the adsorption properties and pore sizes of these materials [7]. Precursors pyrolyzed at 700-1100°C have excellent potential to produce microporous or 'ultramicroporous' (radius < 10 Å) ceramics with good thermal and chemical stability. We

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intend to investigate the porosity of polymer-derived SiC in this intermediate temperature range.

Porosity develops during the heating process that converts the polymer to a ceramic state. The process involves large scale thermal rearrangements and the loss of volatile products (typically 20-60 wt.%). Previous studies [3] have shown that small gas molecules are generated at a rate much greater than their diffusion rate through dense ceramic materials. Consequently, pores and microchannels form as they escape from within the material. However, control of porosity via volatile products has disadvantages. High mass loss precursors lose a large amount of oligomers at $\leq 300^\circ\text{C}$. Oligomer loss would tend to increase the pore size and pore size distribution. The use of organic substituents on the polymer as pore templates [8] in non-oxide systems may leave residual carbon in the ceramic, causing the thermal and chemical stability of the ceramic to be compromised.

Control of thermochemistry of polymer precursors to tailor porosity in SiC is a promising approach. The thermal rearrangement and consolidation of the inorganic network during pyrolysis can be considered analogous to the network forming condensation and gelation process in sol-gel derived [9] oxide ceramics. Control of the collapse of the gel network via precursor structure and reactivity is a powerful tool for tailoring the pore size in SiO_2 [8] and provides precursor-based routes to oxide materials with a variety of pore structures. The principles established for controlling pores and microstructures in silica are important in a number of other metal oxide systems [10]. Are these principles also valid for polymeric non-oxide ceramic precursors? The key difference for non-oxides is that high temperature pyrolysis is necessary for ceramic conversion. In metal alkoxide routes to ceramics the most important steps towards forming the M-O network are low temperature hydrolysis and condensation reactions. In polymer derived non-oxides, the most important steps towards forming the ceramic network are thermal reactions (i.e. via changes occurring above 400°C).

The relative contributions of thermochemical condensation and the evolution of gaseous products to porosity and the ability to control them via polymer structure must be established to determine the ranges of pore sizes and volumes that can be produced from these precursors. Most of the thermal reactions take place through highly reactive intermediates such as radicals. The residual structures should reflect the character of their surrounding environment. On the other hand, the polymer absorbs a large amount of energy over a long period of time and should yield materials with very thermodynamically stable structures.

We hope to investigate these issues by examining the development of porosity from two distinct precursor classes: (1) linear polymers which should pack efficiently and provide a dense initial structure and (2) more branched polymers where steric limitations should impede packing and provide a more open initial structure. If the ultimate pore structures of ceramics from these two precursors are similar it indicates that thermal processes approach similar thermodynamic end points, but if the pore structures are significantly different it indicates that the pore structure is influenced by kinetics and precursor structure.

The procedures of Seyferth et. al. [11] are an excellent starting point for preparing precursors with a variety of structures. Polymethylsilane (PMS) is produced in a two stage process. First, sodium dehalocoupling of methylchlorosilane produces a low molecular weight polymer (reaction 1). Then, this polymer is further cross linked (reaction 2) with Group IV metallocene catalysts that were first developed by Harrod et.al. [12]

Finally, the polymer is pyrolyzed to high purity SiC (> 95% with elemental Si as the primary contaminant) in relatively high ceramic yield (~ 80% of the original polymer mass):

The two stage precursor synthesis allows the adjustment of reaction conditions at a number of stages. Variation of reaction temperature, time, solvent and other reaction parameters provides control over polymer properties.

EXPERIMENTAL

Na coupling of dichlorosilanes involves the use of flammable and highly reactive materials, may involve violent exotherms, and should be approached with caution [14]. Sodium was not purified beyond the removal of the surface oxide layer. Other than the following changes, solvent and reagent purification and general procedures were the same as those published [15]. Dimethylzirconocene (DMZ) was synthesized according to published procedures [13].

Polymer Synthesis:

Low molecular weight polymethylsilane (PMS N) was produced under mixed 7:1 hexane:tetrahydrofuran (THF) solvent conditions [15]. Reaction times of the published procedure were modified as follows: 2-3 h monomer addition, 6 h reaction at 25°C, 12 h of reflux. In a second set of experiments conditions were further modified to include a reflux condenser cooled to -20°C that maximized the product yield by preventing the escape of the volatile monomer (PMS L). Some, low molecular weight PMS samples were catalytically cross-linked with DMZ by refluxing in hexane (PMS NX) [11]. Reflux time was 2 h and solutions contained 2.4 wt% PMS and were .020M in DMZ (1g PMS/ .03g DMZ/ 60ml hexane). Following reflux, the polymers were stored under Ar at -30°C in the original hexane solution to limit further reaction.

Polymer Pyrolysis:

Simultaneous TGA/DTA were performed on a Polymer Laboratories STA 1500. 10-20 mg samples were heated from 25°C to 1100°C under flowing Ar. Bulk samples of 0.6 g to 2 g were pyrolyzed in furnace tubes that could be loaded and handled without exposing the precursor to air. Solid polymers (PMS L) were loaded directly into quartz tubes or boats and fluid, cross-linked polymers (PMS NX) were isolated in quartz tubes from hexane solutions immediately before pyrolysis. Samples were heated under Ar flowing at a constant rate of 5°C/min to various temperatures between 300°C and 1100°C. Samples heated to > 400°C were held at the maximum pyrolysis temperature for 1.5 h while samples heated to ≤400°C were held for 0.8 h because of the product's potential volatility. Char or ceramic yields are based on bulk samples unless otherwise indicated.

Analysis of Pyrolysis Products:

N₂ adsorption isotherms of pyrolysis products were determined at 77K using a Micromeritics ASAP 2000. Surface areas reported were determined using Brunauer-Emmett-Teller (BET) analysis. Gaseous products of a solid polymer (PMS L type) were analyzed by TGA/FTIR with a TA Instruments 2050 Analyzer interfaced with a Bio-Rad FTS 40 FTIR Spectrometer equipped with a mercury cadmium telluride detector cooled to 77K. Microstructure of the powder samples was evaluated with a Siemens Model D-5000 x-ray diffractometer.

RESULTS & DISCUSSION

A comparison of the pyrolysis products of polymers with different structural and physical properties is the primary means of understanding the effects of precursor structure on porosity. Important properties of the samples used in these comparisons are given in Table 1. These samples are also referred to in the experimental section to help the reader better relate precursor properties to synthesis conditions.

Table I. Properties of Polymers used in Pyrolysis and Porosity Studies

Polymer Sample	Monomer Conserved	DMZ X-link	Degree of Cross-Linking#	Physical State	Ceramic Yield
PMS N	No	No	41%	Oil	10%*
PMS NX	No	Yes	50%	Viscous Oil	78%
PMS L	Yes	No	61%	Solid	74%

As determined by ^1H NMR integration. * Based on TGA yield.

Characterization of the polymethylsilanes synthesized in Table I agrees with published results [11,16]. However, product and ceramic yields for PMS N were often lower than those published [11] with product yields often as low as 20%. Strict conservation of the monomer by cooling the reflux condenser to -20°C increases product yields to $\sim 60\%$. The solid, highly cross linked nature (60-70% cross linking) of the products (PMS L) is quite surprising in light of previous work [11,15]. These yellow or gold solids have high ceramic yields, but have limited solubility in hexanes, THF and toluene compared to PMS N or PMS NX. Reaction of PMS N with DMZ increased the degree of cross-linking by 8-12% to form PMS NX. Reaction of PMS L with DMZ did not significantly change the degree of cross-linking or improve its ceramic yield.

Bulk samples of PMS NX and PMS L were heated to various temperatures between 300 and 1000°C . TGA/DTA analysis shows the processes occurring during thermal treatment. Fig. 1 shows the TGA/DTA scans of PMS NX. The very rapid weight loss and

Fig. 1 TGA/DTA Analysis of PMS NX, 25-1200°C. (TGA=Solid Trace)

Fig 2. BET Surface Area of PMS L and PMS NX vs. Pyrolysis Temperature.

endothermic peak below 100°C indicate the loss of solvent from the sample (region I in Fig. 1). A relatively sharp weight loss and a series of exothermic events occur from 200°C – 500°C (region II). The most significant of these DTA peaks is associated with Si-Si bond scission and the transition of the polymer backbone to a polycarbosilane that reaches a maximum at $\sim 450^\circ\text{C}$. A constant gentle weight loss occurs from 600°C – 850°C (region III) and an increase in the rate of loss and an associated exothermic peak begin at about 850°C (region IV). PMS L, followed the same basic trends in rates of weight loss and thermochemistry with some minor differences in events. PMS L gave no solvent loss, but showed a sharp weight loss and a series of exothermic events from 150°C – 550°C . The DTA maximum associated with the Si-Si scission occurs at $\sim 400^\circ\text{C}$. The weight of PMS L remains relatively stable between 700°C and 900°C . At $\sim 900^\circ\text{C}$ an exothermic DTA peak and

an associated weight loss occur but events are narrower and lower in magnitude for PMS L (0.5 wt% lost over a $\sim 75^\circ\text{C}$ range) than for PMS NX (1.5 wt% lost over a $\sim 200^\circ\text{C}$ range).

Fig. 2 shows the BET surface areas of PMS NX and PMS L heated to various temperatures. Materials heated to either 400°C or $800\text{--}900^\circ\text{C}$ followed Type I isotherms that were characteristic of microporous materials with a low volume percent porosity ($\sim 2\text{--}7$ vol.% for PMS L at 866°C). Other pyrolysis temperatures yielded materials dense to N_2 . TGA/FTIR shows three major periods of gas evolution: i. MeSiH_3 from $200\text{--}400^\circ\text{C}$, ii. CH_4 from $375\text{--}575^\circ\text{C}$, and iii. above 625°C a complex spectra with strong C-H signals with some weaker signals that may indicate Si-C or Si-H groups. XRD also indicates significant material changes occurring from $700\text{--}900^\circ\text{C}$. Diffraction patterns of samples heated to $\leq 733^\circ\text{C}$ are amorphous. Crystallization begins near 800°C where broad peaks characteristic of $\beta\text{-SiC}$ first appear. The peaks narrow with further heating but the crystallite size remains small even at 1000°C .

Careful control of synthesis conditions of the SiC precursors have produced polymers with different structures able to provide a variety of packing environments. The highly cross linked products that were produced by conservation of monomer are thought to be due to an increase in the local monomer concentration [16]. Reaction of fluid PMS N with DMZ yielded PMS NX, a polymer with increases in cross-linking and ceramic yield similar to those published [15]. Reaction of highly branched PMS L with DMZ did not produce similar effects. PMS L had relatively limited solubility in hexane. Polymers successfully cross-linked may have precipitated from hexane, or the highly branched nature of the polymer may have prohibited the coordination of two polymers to the Zr center to form the intermediate necessary for cross-linking. Alternate metallocenes and reaction conditions may be able to successfully cross-link these highly branched polymers.

Previous studies[4,7] indicated significant surface areas for precursors heated between 400° and 900°C . The low surface area throughout most of the temperature cycle for the PMS samples may be related to the high ceramic yield of the polymer. Most ceramic precursors contain excess organic groups which are ultimately incorporated into the ceramic and to some degree inhibit crystallization of the network. PMS in the polymer state has a Si:C ratio of 1.0 and contains numerous, reactive Si-H sites. These features lead to high ceramic yields for PMS and more rapid densification and crystallization compared to other precursors. They may also be responsible for the rapid disappearance of surface area observed in these materials. The goal of this research is to develop porous materials with excellent thermal and chemical stability. The porosity that develops above 800°C has the potential to be stable at or near its formation temperatures. Our research efforts have focused on better understanding events above 800°C . Other characterization techniques shed some light on the source of this porosity. TGA/DTA indicates weight loss and exothermic events occurring near the onset of this porosity. TGA/FTIR also shows a maxima in the evolution of gaseous products between 800 and 900°C . There are clear indications of thermochemistry and gaseous products as a potential source of this porosity. XRD shows the onset of crystallization to begin within this regime as well. Local changes in density of the new, small crystallites may be responsible for the development of surface area. A more detailed understanding of the gaseous products and the microstructure is necessary to fully understand and exploit this porosity that develops at high temperatures. The TGA/FTIR used to evaluate the pyrolysis gases cannot detect H_2 which should be an abundant product of the thermal reactions, especially at higher temperatures. Mass Spectrum analysis can provide a more complete picture of all of the gaseous products generated. Quantitative XRD spectra should be collected with special attention paid to both the degree of crystallinity and the crystallite size. These tests may reveal a correlation between the development of porosity and a specific pyrolysis gas or microstructural trend.

A comparison of the development of porosity from the two different polymers shows the materials similar with only slight differences in the development of porosity

from 800-900°C. The porosity of PMS NX seems to develop over a longer temperature range. This may be a reflection of the greater magnitude and longer temperature range of mass loss above 850°C in PMS NX v. PMS L. This trend may be an indication of the importance of gaseous species in the formation of this porosity.

CONCLUSIONS

PMS polymers with different structural and physical properties were synthesized to investigate the effects of precursor structure on the porosity of SiC. Despite the initial structural differences these polymers show very similar trends in weight loss and thermochemistry. N₂ adsorption results indicate the development of the most significant porosity (above 733°C) is not influenced by precursor structure but is the result of high temperature thermochemistry and/or microstructural changes. TGA, DTA, and analysis of pyrolysis gases all are consistent with porosity created via gaseous products but the role of microstructure cannot be ruled out at present. Future work should focus on understanding and controlling these high temperature sources of porosity.

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DEVELOPMENT OF A SHALLOW-FLAW FRACTURE ASSESSMENT METHODOLOGY FOR NUCLEAR REACTOR PRESSURE VESSELS

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Shallow-flaw fracture technology is being developed within the Heavy-Section Steel Technology (HSST) Program for application to the safety assessment of radiation-embrittled nuclear reactor pressure vessels (RPVs) containing postulated shallow flaws. Cleavage fracture in shallow-flaw cruciform beam specimens tested under biaxial loading at temperatures in the lower transition temperature range was shown to be strain-controlled. A strain-based dual-parameter fracture toughness correlation was developed and shown to be capable of predicting the effect of crack-tip constraint on fracture toughness for strain-controlled fracture. A probabilistic fracture mechanics (PFM) model that includes both the properties of the inner-surface stainless-steel cladding and a biaxial shallow-flaw fracture toughness correlation gave a reduction in probability of cleavage initiation of more than two orders of magnitude from an ASME-based reference case.

INTRODUCTION

The loading conditions generated during a pressurized-thermal-shock (PTS) transient are of primary interest for the structural integrity assessment of an RPV pressure boundary. A PTS loading transient produces biaxial pressure and thermal stress fields in the wall of an RPV. Thermal stresses are highest adjacent to the inner surface of the vessel where the effects of irradiation embrittlement and transient temperatures combine to produce the maximum reduction in the material fracture toughness. The net result of this combination of conditions is that the majority of predicted crack initiations originate from shallow flaws located on the inner surface of the RPV (Selby et al (1)). The dominant influence of shallow surface flaws generates the need for a shallow-flaw fracture assessment methodology that incorporates /1/ the effects of reduced crack-tip constraint on material fracture toughness associated with shallow flaws; /2/ the effects of prototypical biaxial stress states on measured fracture toughness data for shallow flaws; /3/ dual-parameter fracture correlations for predicting material fracture toughness of shallow flaws in a biaxial stress field; and /4/ the effects of an inner-surface thin layer of stainless-steel cladding on fracture behavior of shallow surface flaws. This paper provides an overview of recent developments in shallow-flaw fracture technology for RPVs resulting from HSST Program research in these areas.

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FRACTURE TOUGHNESS DATA

Fracture toughness tests have been performed on single-edge notch bend (SENB) test specimens using both deep and shallow flaws (Theiss et al (2), Bass et al (3), and Link and Joyce (4)). Beams tested by ORNL were fabricated from A 533 Grade B Class 1 (A 533 B) material and were nominally 100 mm deep (2). Clad beams cut with a 230 mm square cross section from the RPV of a canceled nuclear plant were tested under the HSST Program (3). Additional shallow-flaw fracture-toughness data for A 533 B material were generated by the Naval Surface Warfare Center (NSWC), in Annapolis, Maryland (4). The NSWC tests were also conducted using large ($B = 89$ mm, $W = 83$ mm) SENB specimens. Figure 1 shows that the shallow-flaw fracture-toughness data from all sources form a homogeneous population when plotted as a function of temperature normalized to the nil-ductility temperature (T_{NDT}). The lower-bound curves for the deep- and shallow-flaw data were shown to be similar (Pennell et al (5)), but the mean fracture-toughness and scatter of data are significantly higher for shallow flaws than for deep flaws.

Pressure and thermal gradient loadings both produce biaxial stress fields in the wall of an RPV. One of the principal stresses is aligned parallel to the crack front of a shallow surface flaw oriented in the longitudinal direction. There is no counterpart of this far-field out-of-plane stress in fracture-toughness tests performed using SENB test specimens with uniaxial loading. Shallow-flaw fracture-toughness of RPV material has been shown to be higher than the deep-flaw fracture-toughness because of the relaxation of crack-tip constraint (2). The far-field out-of-plane stress has the potential to increase stress triaxiality (constraint) at the crack-tip, and thereby reduce the shallow-flaw fracture-toughness enhancement. Therefore, effects of biaxial-loading must be factored into application of shallow-flaw fracture-toughness data to the probabilistic analysis of RPV integrity under PTS loading.

An initial series of biaxial fracture toughness tests (Pennell et al (6)) has been completed using test specimens of the cruciform design shown in Figure 2. This cruciform specimen was specially developed at ORNL to permit the controlled application of biaxial loading, which results in controlled variations of crack-tip constraint for shallow surface flaws. The biaxial load ratio is defined as P_T/P_L , where P_T is the total load applied to the transverse beam arms and P_L is the total load applied to the longitudinal arms. Tests were run with P_T/P_L ratios of 0.0, 0.6, and 1.0. K_{Ic} data from the biaxial tests are shown in Figure 3, plotted as functions of the biaxiality ratio P_T/P_L . The plot shows a decrease in the lower-bound shallow-flaw fracture-toughness with increasing biaxiality ratios. The data also indicate a trend of decreasing data scatter at a stress ratio of 0.6 when compared with the data scatter observed in both the uniaxial ($P_T/P_L = 0$) SENB shallow-flaw tests (see Figure 1) and the biaxial shallow-flaw tests at a P_T/P_L loading ratio of 1.0.

The HSST Program is conducting a series of biaxial cruciform tests (5), (6) to investigate the behavior of shallow, finite-length, through-clad surface flaws where the cladding, temperature, and biaxial load ratio are the primary independent variables. The latter test series is utilizing the same source material as that used for the ORNL full-thickness clad beams specimens (3). In these clad cruciform specimens, the test flaw leading edge passes through the clad material, the HAZ, and, for flaws deeper than approximately 10 mm, into the RPV shell base material.

These tests will help define an envelope of flaw sizes for which cleavage initiation will not be expected under severe PTS type loading. Such an envelope will allow exclusion of such a family of small flaws from probabilistic analyses, potentially contributing to a reduction in the calculated conditional probability of RPV failure.

DUAL-PARAMETER TOUGHNESS CORRELATIONS

Crack-tip constraint is the term used to describe conditions that influence the hydrostatic component of the crack-tip stress field. Dual-parameter fracture-toughness corrections and correlations have been proposed to provide a quantitative assessment of the effect of reduction of crack-tip constraint on fracture-toughness. Stress-based dual-parameter methodologies include the $J-A_{cr}$ fracture-toughness scaling procedure proposed by Dodds et al (7). This methodology utilizes the effect of crack-tip constraint on the in-plane stresses at the crack tip to infer the effect of constraint on fracture-toughness. Prior investigations of biaxial loading effects have concluded that out-of-plane biaxial loading has little effect on in-plane stresses at the crack tip, but does influence the width of the crack-tip plastic zone in the direction of crack propagation (5), (6). Recent elastic-plastic finite element analyses of the biaxial cruciform specimen, using a model with a highly refined treatment of the crack-tip region, have confirmed these conclusions (6). In Figure 4, far-field stress biaxiality is seen to have little effect on the in-plane stresses near the crack tip of the ORNL cruciform specimen. Additional analyses (6) have further confirmed that the stress-based constraint correction procedure described in reference (7) cannot predict the observed effects of biaxial loading on shallow-flaw fracture-toughness.

Wells (8) proposed that initiation of cleavage fracture is controlled by strains in the crack-tip region reaching a critical value. Adopting a strip-yield model, he studied the hypothesis that initiation of brittle fracture is uniquely determined by a critical value, δ_c , of the crack-tip opening displacement (CTOD). For plane stress conditions, he developed relationships between CTOD, δ , the plastic zone width in the plane of the crack, R_{pl} , and overall plastic strain, for loading conditions that range from below to above general yielding. Beyond general yielding, he postulated that δ becomes proportional to the plastic strain taken over some gauge length spanning the fully plastic area of the specimen.

As previously noted, a second (or dual) correlation parameter must also be introduced into the cleavage fracture model to quantify loss-of-constraint or departure from small-scale yielding conditions. The case for using R_{pl} in a strain-based fracture-toughness correlation derives from the observation that the CTOD (δ) is a function of R_{pl} and that this relationship is constraint-dependent. The δ vs R_{pl} relationship has been studied by ORNL (5) for general beyond-plane-strain boundary conditions, for both contained and uncontained yielding, using test data from the biaxial cruciform testing program. A linear relationship between $\sqrt{\delta_c}$ and $\ln(R_{pl})$ was determined from 3-D finite element analysis of the biaxial test results at cleavage fracture initiation and is given by

$$\sqrt{\delta_c} = 1.909 + 0.189 \ln(R_{pl}) \quad (1)$$

and shown in Figure 5. Also in Figure 5, the $\sqrt{\delta}$ vs $\ln(R_{pl})$ loading trajectories for three biaxial loading ratios (i.e., $P_T/P_L = 0, 0.6, \text{ and } 1$) are superposed on the

fracture toughness locus of Equation 1, together with fracture-toughness data points obtained from the cruciform specimens. These loading trajectories were generated using a modified version of the Wells relation for δ given by (8)

$$\delta = \pi \bar{\epsilon} R_{pl} \quad (2)$$

where

$$\bar{\epsilon} = \frac{1}{R_{pl}} \int_0^{R_{pl}} \epsilon_{33} dr \quad (3)$$

In Equation 2, the integrated average of the opening-mode strain, $\bar{\epsilon}$, taken over R_{pl} , replaces a quantity in reference (8) defined as the overall tensile strain. Variations of $\bar{\epsilon}$ with longitudinal load, obtained from 3-D finite-element analysis of three biaxial loading cases, $P_T/P_L = 0, 0.6$, and 1, are given in Figure 6. These $\bar{\epsilon}$ vs load relations were used in Equation 2, along with calculated values of R_{pl} , to compute the predicted loading trajectories given in Figure 5. These results confirm that a measure of the opening-mode strain field in the near-crack-tip ligament is capable of differentiating among the applied biaxial loading ratios to predict variations in biaxial loading trajectories. The linearity of the K_J vs $\sqrt{\delta}$ relationship is preserved under the full range of biaxial loading ratios. Thus, results for the loading trajectories and fracture toughness locus for the cruciform testing program can be restated in terms of equivalent K_J , K_{Jc} vs $\ln(R_{pl})$ relationships (5).

In Figure 5, intersection of these nonlinear trajectories with the linear toughness locus is governed by the dependence of the trajectories on constraint as influenced by the biaxial loading ratio. Unique toughness values are predicted for the uniaxial ($P_T/P_L=0$) and biaxial ($P_T/P_L=0.6$) loading cases. The intersection of the trajectory for equibiaxial ($P_T/P_L=1$) loading with the toughness locus predicts both low and high toughness values for this loading condition. In fact, these low and high toughness values were realized in tests of the biaxial ($P_T/P_L=1$) loading case. Uncontained yielding that developed in two of the biaxial ($P_T/P_L=1$) tests gave high toughness values that were similar to those of the uniaxial loading tests. Collectively, the results depicted in Figures 5-6 confirm that $\ln(R_{pl})$ is a viable second parameter for characterizing strain-controlled fracture.

CLAD MODELING AND BIAXIAL LOADING EFFECTS ON RPV PFM ASSESSMENTS

Commercial nuclear pressurized-water reactors in the United States are constructed with a thin stainless-steel layer of cladding on the inner surface of the vessel. The primary purpose of this cladding is to minimize the volume of corrosion product entering the primary system coolant. Shallow flaws having depths on the order of the combined thickness of the cladding and HAZ dominate the frequency distribution of flaws assumed in probabilistic fracture mechanics (PFM) assessments of RPVs (1). Behavior of these shallow flaws during a PTS transient clearly would be influenced by the material/fracture properties and mechanical interactions associated with the elements that comprise the clad overlay structure.

Analyses of a representative RPV were performed to determine the sensitivity of the conditional probability of crack initiation, designated as $P(\text{IIE})$, to the effects of clad modeling and biaxial loading. Specific refinements were introduced into clad models to take account of a low clad yield stress, and a high clad ductility that precludes initiation in the clad layer. Probabilistic assessments were carried out for axially-oriented finite-length inner surface flaws with an aspect ratio of 2, as well as for 2-D flaws. These PFM analyses considered fifteen discrete flaw depths evenly spaced in a region extending 50 mm from the inner surface of the RPV. The flaw sizes were stochastically simulated as predicted by the Marshall flaw depth distribution function. Loading of the vessel was provided by stylized thermal transients of varying severity that are governed by the final coolant temperature, T_f .

The PFM analyses required that mean-, upper-, and lower-bound fracture-initiation-toughness curves be defined. In the Monte Carlo analysis process, fracture-initiation toughness is stochastically sampled for each simulated initial flaw depth. There is not a sufficient number of experimental shallow-flaw biaxial K_{Jc} data points from which to derive a statistically meaningful mean K_{Jc} curve. Thus, statistically derived lower-bound and mean curves from the shallow-flaw uniaxial K_{Jc} database were adjusted, based on the limited biaxial data, to account for biaxial effects. Figure 7 illustrates the statistically derived mean curve for the shallow-flaw uniaxial K_{Jc} database given in Figure 1. Primary characteristics of this fracture-initiation toughness database are a higher mean value and increased variability, particularly in the transition region. A lower-bound fracture toughness ratio (biaxial/uniaxial) of 0.57 was obtained in HSST program tests with uniaxial and biaxial loading. Therefore, the lower-bound curve for shallow-flaw biaxial loading was established by shifting lower-bound uniaxial curve down by 43 percent. The resulting shallow-flaw biaxial lower-bound K_{Jc} curve is shown in Figure 7. For reference, Figure 7 also includes the ASME K_{Ic} curve. Based on biaxial data in Figure 3, an upper-bound shallow-flaw biaxial curve was derived by adjusting the shallow-flaw uniaxial upper-bound curve down by 3 percent. Also, in Figure 7, the mean curve for shallow-flaw biaxial loading was taken as equidistant between the lower- and upper-bound curves.

The conditional probability of crack initiation vs T_f was computed for a reference case of an embrittled RPV described in reference (5), i.e., an ASME-based fracture toughness correlation, an LEFM model, cladding toughness equal to that of base metal, and a 2-D flaw assumption. Results for this reference case are given as curve 1 in Figure 8. Elements of the reference model were changed separately to determine the corresponding change in conditional probability of initiation for PTS transients of varying severity (all modified cases assumed a semicircular flaw). If the 2-D flaw in the reference model is replaced by a semicircular flaw, a more severe probability of initiation is predicted for a range of higher final coolant temperatures (curve 2 of Figure 8). An approximation for effects of clad plasticity was employed which does not allow the stress in the clad thickness to exceed 379 MPa (model EPFM in Figure 8). High clad ductility is incorporated by not allowing cleavage initiation to occur at any discrete angular location on the crack front that resides in the clad region. Also, fracture toughness correlations based on uniaxial and biaxial shallow-flaw toughness data sets from Figure 7 were considered, in addition to the ASME-based correlations. The combined effects of clad yielding and clad toughness properties provided a decrease in initiation probabilities (from the reference case) of

as much as one order of magnitude over the range of final coolant temperatures (curve 3 in Figure 8). When a uniaxial shallow-flaw toughness correlation is adjusted for biaxial effects, the resultant correlation provides initiation probabilities between one and two orders of magnitude lower than those from the ASME-based correlation (curve 4 in Figure 8). The combined-effects model that includes both the cladding properties and the biaxial shallow-flaw toughness correlation gave the maximum reduction of more than two orders of magnitude from the LEFM-ASME-based correlation (curve 5 in Figure 8).

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Figure 1 Shallow-flaw toughness data for A533 B Plate and weld material.

Figure 3 Shallow-flaw toughness data for a single heat of A533 B steel.

Figure 2 Conceptual features of the cruciform test specimen.

Figure 4 Far-field stress biaxiality effects on in-plane stresses near crack tip.

Figure 5 Dependence of $\sqrt{\delta} - \ln(R_{pl})$ loading trajectories on biaxiality ratio.

Figure 7 K_{Jc} curves adjusted for effect of biaxiality on shallow-flaw toughness.

Figure 6 Dependence of opening mode strain on load and biaxiality ratio.

Figure 8 Conditional probability of crack initiation vs final coolant temperature.