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A Progress Report on the project

entitled

FABRICATION, PHASE TRANSFORMATION STUDIES AND CHARACTERIZATION OF SiC-AlN-Al_2OC CERAMICS

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ABSTRACT

SiC and AlN are two of the important high temperature structural ceramics. AlN and the 2H polytype of SiC are isostructural. Prior work has shown that they form an extensive solid solution at temperatures ≥ 2000°C. At lower temperatures, the solid solution can undergo phase separation. Additionally, Al_2OC is also isostructural and can form extensive solid solutions with SiC and AlN. The formation of solid solutions in such refractory materials as well as the tendency to undergo diffusional phase transformations suggests that a potential exists to improve properties through alloying. The principal objective of the proposed work is to examine phase relations, phase transformations, the resulting precipitate morphologies and their influence on mechanical properties of SiC-AlN-Al_2OC ceramics. Formation of modulated structures have been documented in SiC-AlN ceramics in our work. It has been shown that modulations occur along directions other than the [0001] direction and this results in the formation of a tweed type of a microstructure. In the AlN-Al_2OC system, the occurrence of cellular precipitates as well as coherent, disc-shaped precipitates has been observed.

During the past year, work has progressed in the following areas: (1) Phase separation in SiC-AlN system: The effect of coherency strain energy on the precipitate morphology. (2) High temperature creep of SiC-AlN ceramics containing modulated structures and SiC-Al_2OC ceramics. (3) Fabrication and characterization of damage-resistant SiC-AlN ceramics. Three manuscripts have been submitted for publication. Preprints of these are included as appendices. One manuscript has appeared in print. A reprint is included as an appendix.

It is proposed that the work on the effect of coherency strain energy on morphology will be continued. Morphology of phase separation will be examined along several axes by TEM and will be compared with images generated by computer simulation. The effect of coherency strain energy on precipitation in AlN-Al_2OC system will be examined. Of specific interest is the strain-induced lattice parameter changes and the precipitate shapes. Finally, experiments will be conducted to examine interdiffusion in SiC-AlN and AlN-Al_2OC solid solutions. The objective is to determine if interdiffusion in AlN-Al_2OC is faster than that in SiC-AlN. Experimental work will consist of sample fabrication, thermal treatments, TEM, X-ray diffraction, and electron microprobe analysis.

I. PROGRESS REPORT

Progress during the past year is described briefly in the following paragraphs. Preprints/reprints of the manuscripts during the past year are attached here as appendices. The titles of the manuscripts are as follows:

1) S-Y Kuo and A. V. Virkar, "Morphology of Phase Separation in AlN-Al_2OC and SiC-AlN Ceramics", *J. Am. Ceram. Soc.*, **73** [9] 2640-2646 (1990).

2) "High Temperature Creep of SiC Densified Using a Transient Liquid Phase", Z. C. Jou, A. V. Virkar, and R. A. Cutler, to appear in *J. Mater. Res.* **6** [9] (1991).

3) "Phase Transformation in SiC-AlN Pseudobinary System: The Role of Coherency Strain Energy", J. Chen, Q. Tian, and A. V. Virkar, submitted to the *J. Am. Ceram. Soc.*, (1991).

4) "Damage-Resistant SiC-AlN Layered Composites with Surface Compressive Stresses", by R. Sathyamoorthy, A. V. Virkar, and R. A. Cutler, submitted to the *J. Am. Ceram. Soc.*, (1991).

Currently, two more manuscripts are under preparation; one on creep of SiC-AlN and the other on phase separation in AlN-Al_2OC.

<u>I.(a): The Effect of Coherency Strain Energy on the Morphology of Phase Separation in SiC-AlN:</u> Substantial effort was devoted to identifying the nature and mechanism of the formation of modulated structures in SiC-AlN. This effort consisted of two main approaches: (i) Examination of modulated structures by TEM, (ii) Theoretical analysis of coherency strain energy and computer simulation of microstructures assuming the occurrence of phase separation by spinodal decomposition. The principal accomplishment of this work can be summarized as follows:

(1) It was identified that modulations occur orthogonal to $\{012\}$ (or $\{01\underline{1}2\}$ on a four index system) type of planes. Using two beam condition, it was demonstrated that the tweed structure results due to the occurrence of modulations in more than one direction. By imaging through (012) and $(0\underline{1}2)$ reflections, one dimensional modulations were highlighted.

(2) The modulation wavelength was correlated with the distance between the satellite spots and the main reflections.

(3) Coherency strain energy was calculated from first principles. It was demonstrated that the calculated elastic energy, F_{el}, was similar to the elastic energy function, Y(n), of Mayo and Tsakalakos [1]. The minimum in F_{el} vs. θ where θ is the angle with respect to the c-axis exhibits a minimum at about $\theta \approx 49^o$. Modulations are expected to occur along this direction. This is in good agreement with experimental observations.

(4) According to the analysis of Mayo and Tsakalakos [1], modulated structures should not occur along directions other than [001] in hexagonal structures. They arrived at this conclusion on the basis of elastic isotropy in the basal plane. However, our experimental results demonstrate that modulated structures do form along arbitrary directions. This apparent discrepancy was rationalized on the premise that elastic isotropy does not imply cylindrical symmetry. That is, not all directions making an angle θ with respect to the c-axis, are equivalent. Specifically, in a hexagonal lattice, for a given θ, there are six equivalent directions. This means that one must replace the integral given by Mayo and Tsakalakos [1] by a summation. When this is done, it is readily shown that modulated structures are predicted on a theoretical basis. This aspect is discussed in detail in Appendix-3.

(5) Computer simulation was conducted following the method described by Cahn [2] for cubic structures assuming the occurrence of phase separation by spinodal decomposition. The computer generated image of the microstructure was observed to be in excellent agreement with that observed experimentally. Figure #1 compares the actual TEM image with the computer generated image. Details of the computer simulation are described in detail in Appendix-3.

I(b). Creep of SiC-AlN Ceramics Containing Modulated Structures: Phase separation leading to extremely fine and coherent precipitates has been demonstrated in our work. In metallic materials, the effect of coherent precipitates in precipitation strengthening is well known. The obvious question is whether such effects can be observed in highly refractory structural ceramics such as SiC-AlN. The effect of precipitates is expected only at elevated temperatures where either diffusional processes and/or significant dislocation activity is possible. Therefore,

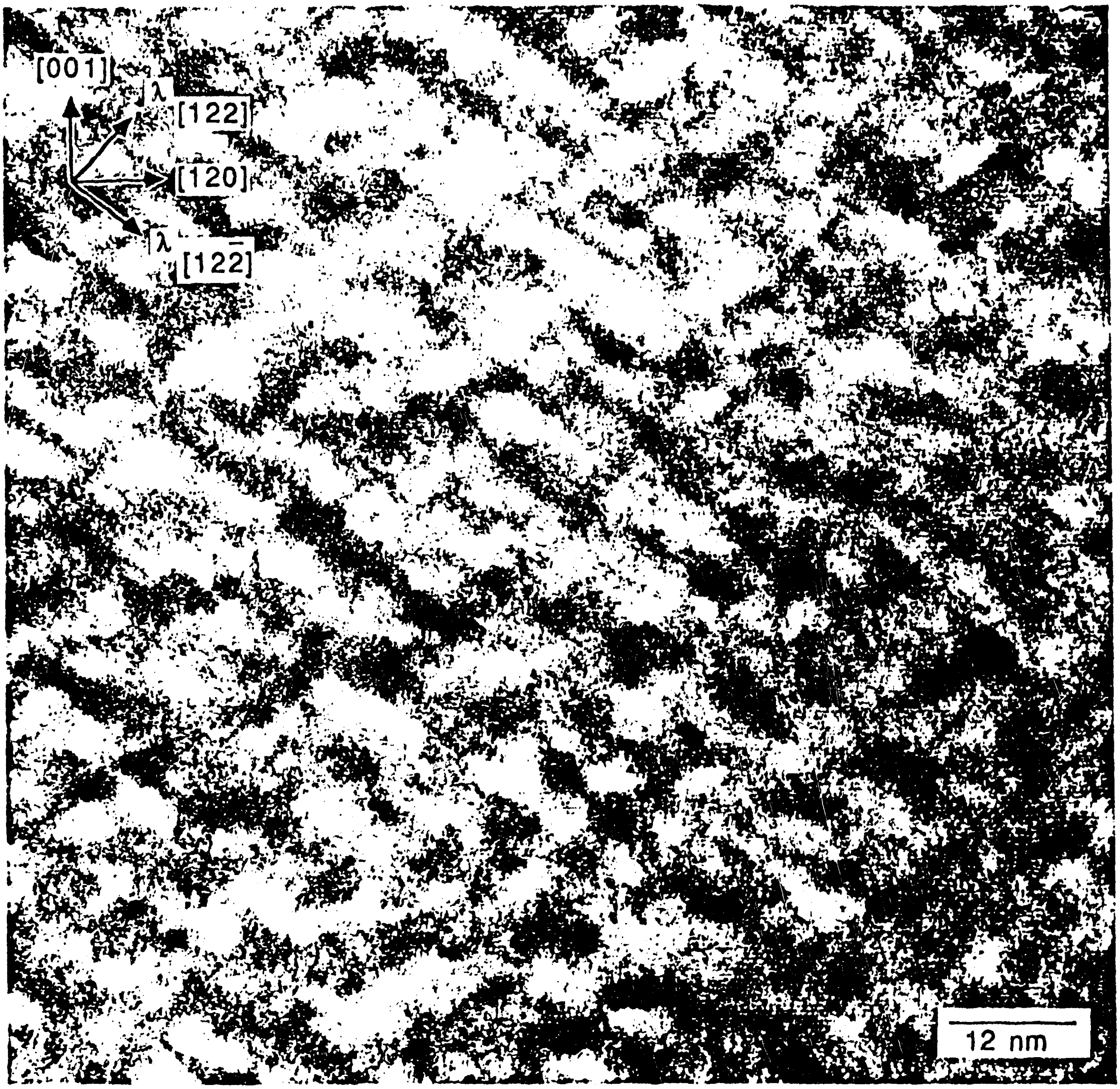

Figure #1(a): TEM high resolution image of SiC-AlN annealed at 1600°C for 320 hours.

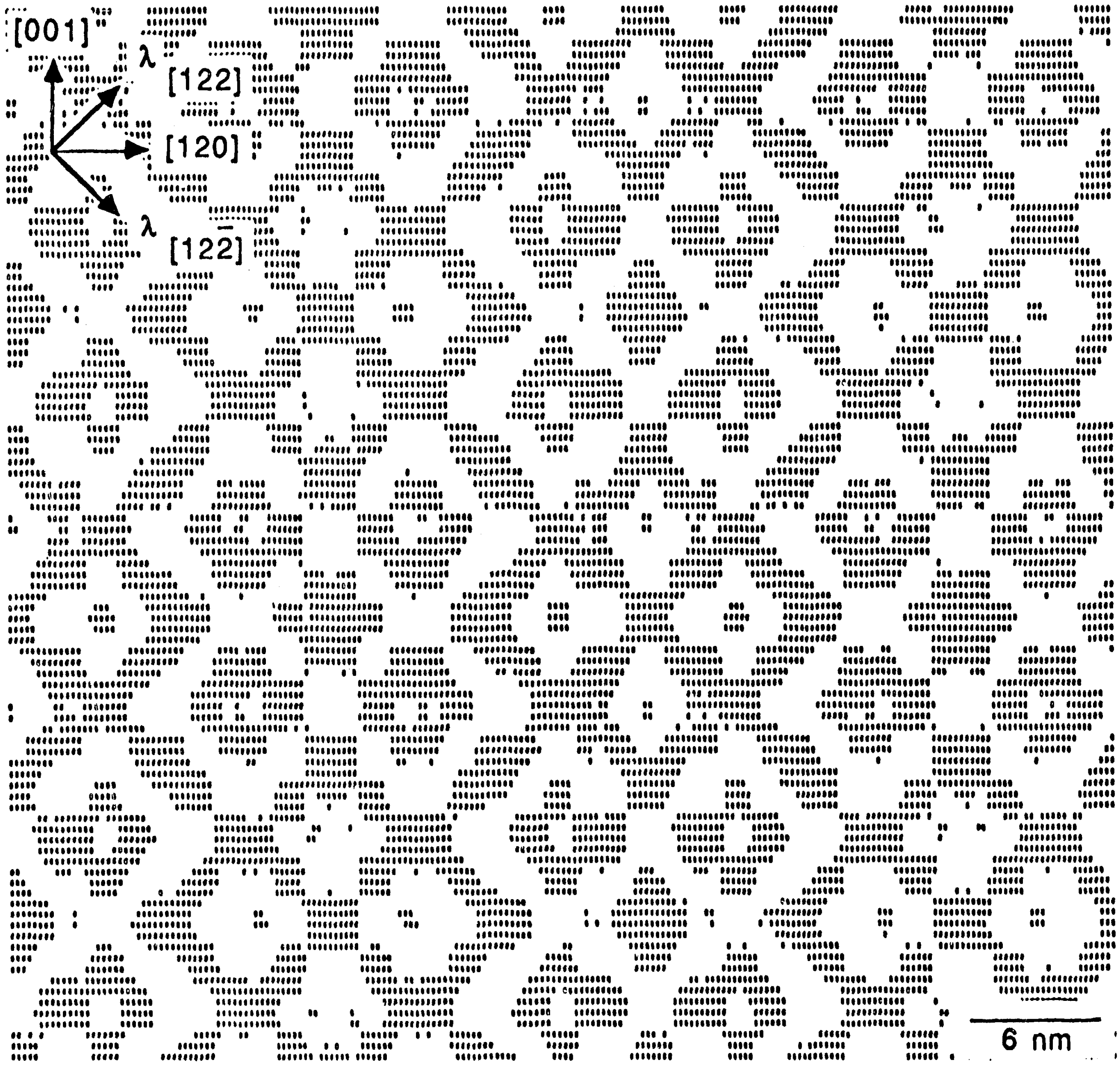

Figure #1(b): A computer-generated image of the morphology of phase separation.

it is expected that any effect of modulated structures will be observable in high temperature phenomena such as creep. A study was undertaken to examine creep behavior of solid solution and spinodally decomposed SiC-AlN of equimolar composition. A manuscript based on this work is under preparation. A brief description of the results is given below.

SiC-AlN samples of equimolar composition were fabricated by hot-pressing at ≥ 2300°C to ensure the formation of a homogeneous solid solution. Some of the samples were annealed at ~1950°C for 100 hours to effect the formation of modulated structures. Figure #2 shows a TEM bright field image of an annealed sample exhibiting modulated structure. Creep in four point bending was measured at temperatures as high as ~1700°C. Figure #3 compares creep rate vs. temperature plots of SiC-AlN solid solution and spinodally decomposed structure with α-SiC. The creep rate of spinodally decomposed SiC-AlN is significantly lower than that of the solid solution of essentially the same grain size. Thus, the precipitates do appear to impede the creep process. Stress exponents were typically in excess of 2.2 indicating that dislocation climb/glide processes must be contributing to the creep. It appears that coherent precipitates do enhance creep resistance, perhaps by dislocation-precipitate interactions.

I.(c): Damage-Resistant SiC-AlN Layered Ceramics: Interest in SiC-AlN system stems from the possibility of developing materials with improved properties through alloying. SiC-AlN has been shown to provide an ideal system to examine fundamentals of phase equilibria and phase transformation mechanisms in this system of practical interest. The objective of this part of the work in the general theme of characterization of structural ceramics containing SiC was to exploit variation of thermal expansion with composition to fabricate damage-resistant layered structures. Our prior work on Al_2O_3-ZrO_2 system [3-6] has shown that layered samples containing monoclinic zirconia in outer layers provides excellent resistance indenation-induced damage. SiC has lower coefficient of thermal expansion compared to AlN and also has greater oxidation resistance. Creep resistance of both materials is excellent. Layered structures containing outer layers rich in SiC were fabricated. Vicker's indentations were introduced into the samples and samples were fractured in flexure. The layered SiC-AlN samples exhibited a substantial resistance to contact-induced damage. This work thus showed that SiC-AlN ceramics are potential structural ceramics for critical applications. A manuscript based on this work is given in Appendix-4.

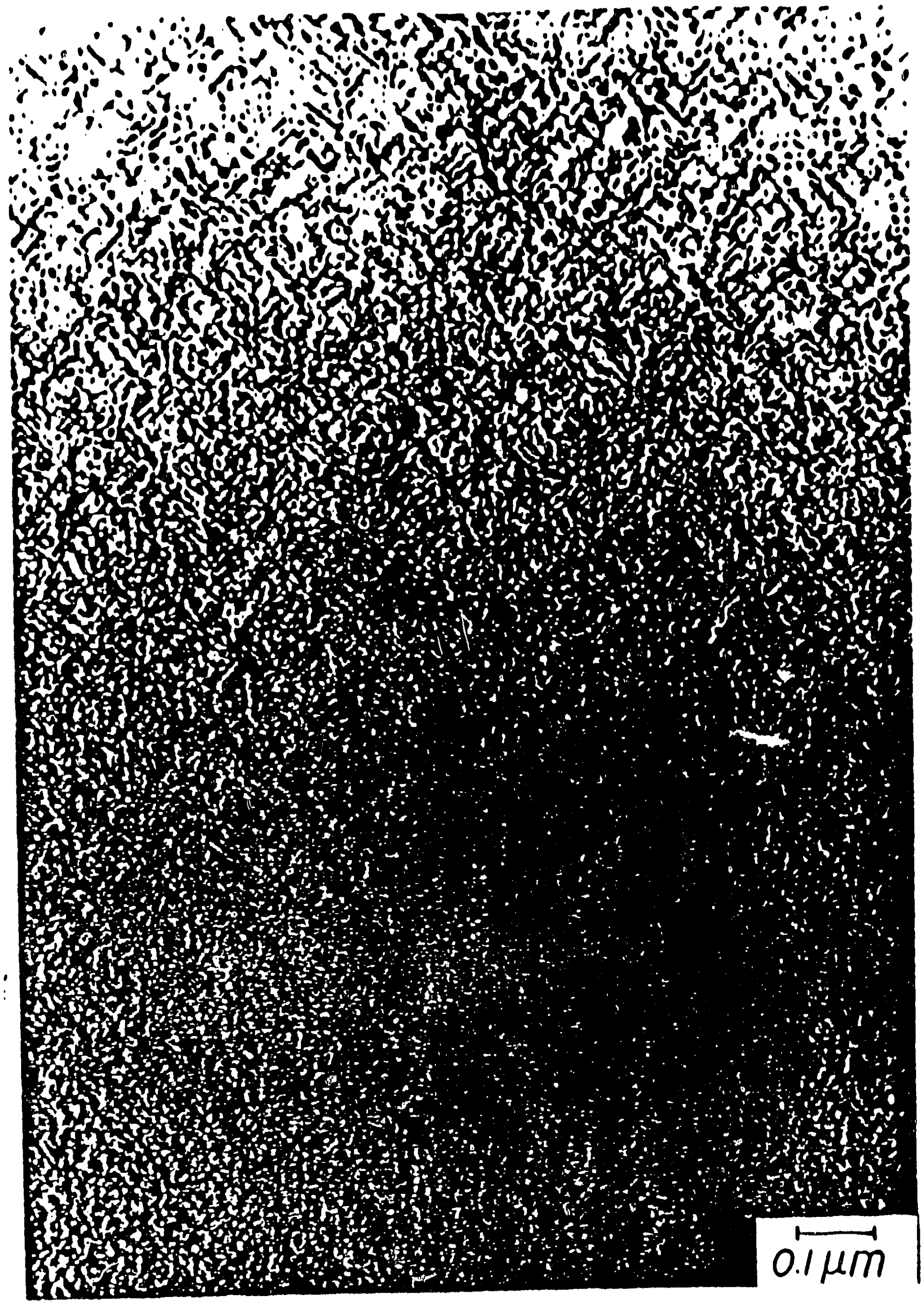

Figure #2: A TEM image of SiC-AlN of equimolar composition annealed at 1950°C for 100 hours.

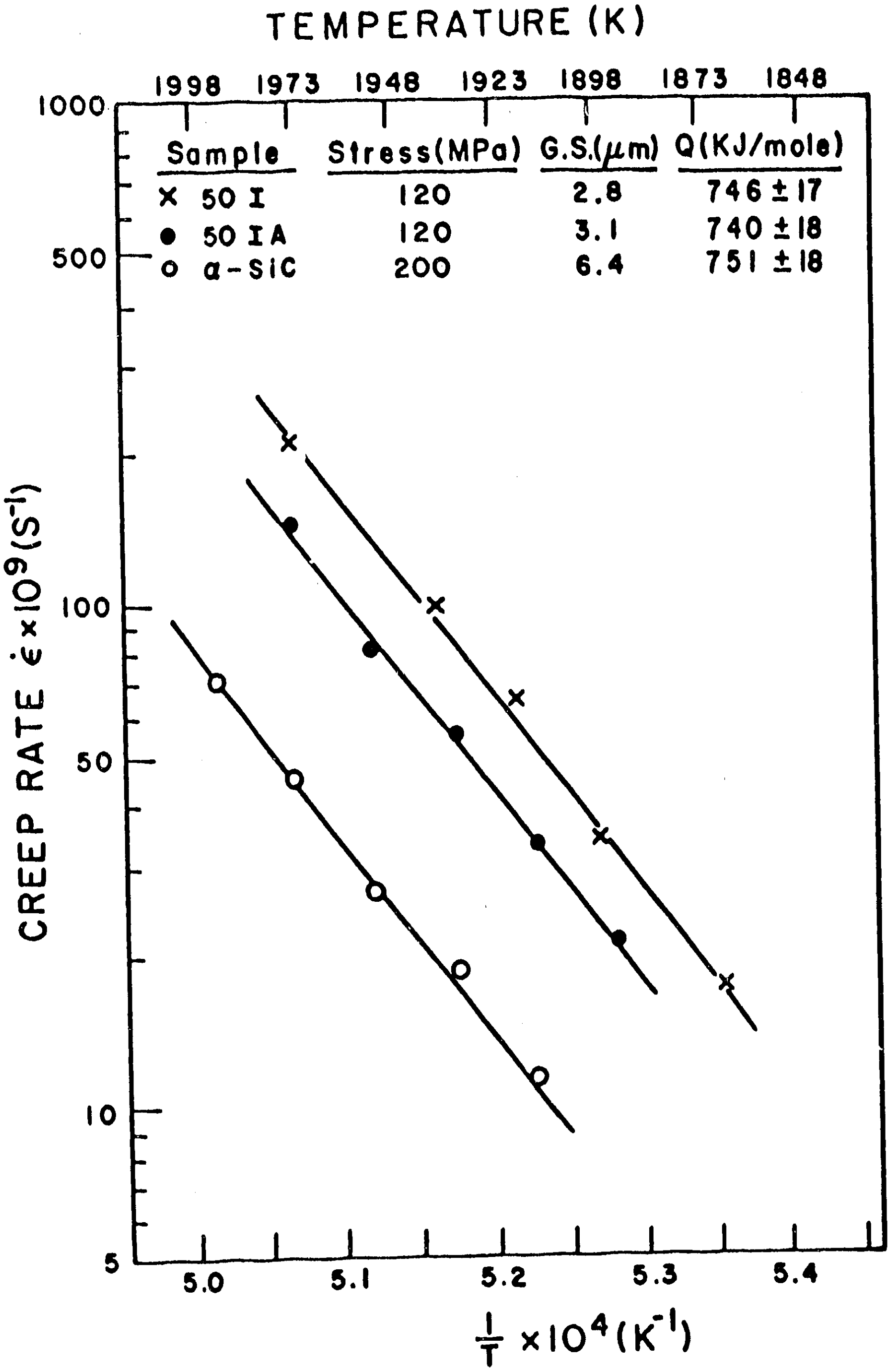

Figure #3: Plots of log(creep rate) vs. 1/T for SiC-AlN solid solution, spinodally decomposed SiC-AlN, and α-SiC.

III. REFERENCES

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3) A. V. Virkar, 'Ceramic Bodies Having a Plurality of Stress Zones', U. S. Patent No. 4,656,071; Date: April 7, 1987.

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6) A. V. Virkar, J. F. Jue, J. J. Hansen, and R. A. Cutler, *J. Am. Ceram. Soc.*, **71** [3] C148-C151 (1988).

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