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論 文 内 容 要 旨

In materials science we conventionally divide materials into distinct classes. Solid materials are primarily classified into the three broad families: metals, ceramics, polymers, and hybrids-composite materials made by combining more than one of the others. Ceramic materials have become increasingly important in our modern world due to their abundant application areas in addition to traditional usages such as tableware, pottery, tiles. These applications based on the wide range of properties of ceramics: high strength, corrosion resistance, wear resistance, low thermal conductivity, favorable optical, electrical or magnetic properties, biological compatibility. On the other hand, we have to face the serious problems in using the unique physical properties of ceramic materials. The major drawback of ceramics is the brittleness, i.e. failure without preceding plastic deformation. At room temperature, they usually fail in a sudden manner of crush before yield. This is the unavoidable problem of ceramics in application of structural materials. Most ceramic materials undergo plastic deformation at high temperature. Macroscopic compression experiments of ceramics indicate a change in deformation mechanisms from brittle to ductile at high temperature. In order to achieve the brittle to ductile transition at room temperature, a hydrostatic pressure component must be imposed to prevent brittle fracture.

High-strength ceramics are of great of interest for application as structural materials due to their excellent mechanical properties. The high-performance ceramics exhibit relative higher strength and lower density compared to metals. This feature is very attractive in areas of structure materials. In addition, most of them under extreme high pressure can withstand high failure strength and exhibit inelastic deformation at room temperature. This feature is a key point for application of structure ceramics. Nevertheless, the

underlying mechanisms of deformation and failure subjected to high pressures are not fully understood due to the complexity of deformation under pressures. For example, the emergence of dislocation slip or twinning in Al_2O_3 and SiC , and the high-pressure phase transformations in Si , Ge , and AlN have been observed. In order to exploring the underlying mechanisms of deformation and failure of high-strength ceramics subjected to high pressures, the high pressure behaviors of three typical high-strength ceramics including B_4C , AlON , and AlN were systematically studied. Nanoindentation and diamond anvil cell are used to conduct a high pressure to the samples. With assistance of Raman spectroscopy, vibrational behaviors of lattice under pressures can be obtained. The pressure-induced structure changes are studied by SEM and TEM.

Firstly, structure evolution of single-crystal B_4C under pressures was systematically investigated by in situ high-pressure Raman spectroscopy. Although recent studies have demonstrated that the localized amorphization in B_4C was formed by nonhydrostatic pressures, unusual intensity changes of B_4C Raman bands at a pressure of ~ 20 GPa is poorly understood. A first-order phase transition (rhombohedral to wurtzite) at high pressures was suggested. In this work, the polarized and resonant Raman scattering of single-crystal B_4C under pressures were systematically investigate in diamond anvil cell. The most noticeable changes are the sharpening and intensity increase of the 270 and 1086 cm^{-1} bands at the pressure above ~ 20 GPa. The pressure-induced intensity change of the 1086 cm^{-1} band (the breathing mode of the icosahedra) is mainly due to the resonance between excitation energy and electronic transition, whereas the intensity change of 270 cm^{-1} band (the chain-icosahedral linkages (A_{1g})) is caused by the depolarization effect. The variations of depolarization ratios of the 270 cm^{-1} band with respect to increasing pressures reflects the symmetric vibration changes from isotropic to anisotropic. This can be attributed to the “wrong” geometry to a small violation of the selection rules coming from the changes in the local ordering at the linkages between icosahedra and chains. The first-order phase transition suggested before has not been found and the pressure-induced lattice distortion can be recovered after removing the quasi-hydrostatic stresses. The larger fracture toughness of nanocrystalline B_4C compared to single crystal B_4C indicates that the ductility of B_4C is greatly improved by refining the grain size. The results of nanoindentation-induced deformation and failure of nanocrystalline B_4C indicates that localized amorphization which is the dominate deformation mechanism of single crystal and micron-level grain sized B_4C doesn't occur in nanocrystalline B_4C . Inelastic deformation in the nanocrystalline B_4C are mainly due to microcracking and grain boundary sliding.

Secondly, aluminum oxynitride spinel ceramic, commercially named as AlON , is attractive as a

transparent structural ceramic against high impact pressures. The mechanical response of AlON under pressures may involve unusual structural changes, such as solid-state phase transition (spinel-type structure to CaTi₂O₄-type structure) and the underlying mechanisms responsible for deformation and failure are not clear. In view of the complicity of the actual deformation and damage mechanisms that lead to the AlON failure subjected to high pressures, a technique of depth-sensitive nanoindentation combined with micro-Raman spectroscopy and TEM is used. In the present study, plastic deformation and failure of AlON are introduced by nanoindentation with a Berkovich indenter. Formation of high density dislocations underneath indentations of AlON, suggesting extensive plastic deformation takes place at high pressure. The discrete displacement bursts observed in loading segments of load-depth curve are due to the generation/propagation of cracks and dislocation-slip system. Fracture toughness was evaluated by measuring the crack length in SEM. TEM observation indicates that cracks oriented along well defined crystallographic planes. Detectable high-pressure phase transition has not been observed by means of Raman micro-spectroscopy and TEM. AlON exhibits obvious anisotropy in mechanical properties. The local mechanical performances changes in the individual grains because of the difference of local crystal lattice orientation.

Thirdly, AlN are being used increasingly in structural applications and particular attention has been paid to its mechanical response under pressures. The inelastic deformation performance in AlN exhibits a transition from elastic behavior at ambient pressures to a plastic response at high pressures, which is an amazing property for a brittle ceramic. In this work, nanoindentation and diamond anvil cell are used to conduct a high pressure to the polycrystalline and single crystal (with different orientations with a surface parallel to basal plane (0001) and side plane (10 $\bar{1}0$)) AlN. The mechanical properties and vibrational behaviors of lattice under pressures can be obtained, respectively. The pressure-induced structure changes are studied by SEM and TEM. Formation of high density dislocations suggests extensive plastic deformation takes place at high pressures in both orientations of single crystal AlN. Pyramidal and prismatic slip systems can be easily activated by external stress. Single crystal AlN exhibits obvious anisotropy in mechanical properties. E and H values are lower on side plane than on the basal plane. The pressure-induced evolution of lattice vibration of AlN crystal was in situ monitored by Raman spectroscopy in diamond anvil cell. The larger pressure coefficient of E₂² mode (vibrations of N atoms in plain) when compressed on side plane suggests a small resistance for deformation and phase transition. Importantly, the plastic deformation of single crystal AlN was firstly observed without confining pressure. This phenomenon is achieved in the compression test of micropillars free-standing on basal plane and side plane prepared by using FIB milling technique.

Stress-strain curves derived from micro-compression tests performed on pillars demonstrate anisotropy in yield strength and plastic behavior for AlN single crystal. The observed yielding stress is attributed to generation of dislocations from perfect crystal. Once dislocations are nucleated at a yielding point, the subsequent plastic deformation related to dislocation propagation will take place. In both orientations, the pressure at the middle of the pillars can not induce the phase transition since the yield stress is much lower than 20 GPa. This is attributed to the stress relaxation by the dislocation nucleation before the phase transformation occurs.

As described above, this thesis was focus on the high pressure behaviors of high-strength ceramics and explores the mechanisms of deformation and failure under high pressures at room temperature. Three kinds of typical high-strength ceramics with different crystal structures have been systematically studied by diamond anvil cell and nanoindentation. All of them under extreme high pressure can exhibit inelastic deformation.

論文審査結果の要旨

高強度セラミックスは、その優れた機械的特性を兼ね備えており構造用材料として注目されている。高圧力の付加状態において、高い降伏強度を有しており、室温において非弾性変形挙動を示すことがわかっていた。しかしながら、その変形と破壊のメカニズムについては高圧環境下における変形の複雑さのために十分理解されていなかった。この学位論文では、高圧環境下における高強度セラミックスの変形と破壊のメカニズムを明らかにするために、 B_4C 、 $AlON$ 、 AlN の3つの高強度セラミックスについて、高圧環境下における挙動を系統的に調べている。ラマン分光法を用いることで、高圧環境下における結晶の振動モードを測定できることを示し、圧力誘起構造変化について、走査顕微鏡(SEM)と透過電子顕微鏡(TEM)を用いて系統的な調査を行っている。論文は6つの章で構成されている。

第1章では、この研究の背景と目的が書かれている。

第2章では、材料作製方法とその評価方法について記載されている。

第3章では、ダイヤモンドアンビルセルを用いて、単結晶 B_4C の高圧環境下における偏光ならびに共鳴ラマン分光スペクトルを系統的に調べている。ナノ結晶 B_4C の機械特性についてナノインデンテーションを用いて評価している。塑性変形に関連した形状変化や構造変化を SEM と TEM を用いて評価している。

第4章では、Berkovich 型の圧子を用いたナノインデンテーションによって導入された $AlON$ の塑性変形と破壊について調査している。ラマン分光法をもちいて、可能性のある相変態の同定を行っている。結晶方位が異なる個々の粒界内における局所的な機械的応答を調査している。

第5章では、ナノインデンテーションとダイヤモンドアンビルセルを用いて、多結晶と単結晶 AlN の高圧環境下における挙動を調査している。高圧環境下における機械特性と結晶の振動モードをそれぞれ得ている。圧力誘起構造変化を SEM と TEM によって評価している。

第6章では、結果のまとめと結言について書かれている。

上記の通り、この学位論文では高強度セラミックスの高圧環境下における挙動に焦点をあて、室温・高圧力下における塑性変形と破壊のメカニズムについて系統的な研究を行っている。これらの結果は、次世代の高強度セラミックスの開発のための重要な指針になっており、学術的評価は極めて高い。

よって、本論文は博士(工学)の学位論文として合格と認める。