soly. process in SiC was carried out taking account of the electron–hole interaction. The partial mole heat of Al dissolving in SiC was detd. on the basis of the thermodn. anal. of the interaction process in the system SiC–Al, on the dependence of Al soly. in SiC on the temp., as well as on the calcn. of the Fermi level, and other parameters.

97: 132190z **Water transfer in a saturated ceramic body with saturated and unsaturated surfaces.** Havrda, Jiri; Oujiri, Frantisek (Vys. Sk. Chem.-Technol., 166 28 Prague, 6 Czech.). *Silikaty (Prague)* **1982,** 26(2), 107–13 (Czech). The diffusion coeff. of water in a satd. ceramic body was detd. (1) by the diffusion couple method and (2) by the method of quasistationary drying. The diffusion couples were constructed (1a) from two satd. bodies or (1b) from the satd. body and one unsatd. body. The diffusion coeff. for drying was detd. either (2a) from the moisture profile in the body or (2b) from the rate of drying. The diffusion coeff. in a satd. body was independent of moisture content even when the other couple body was unsatd. The diffusion coeff. value established by methods (1b), (2a), and (2b) was identical at a given temp. In contrast to this, the diffusion coeff. value established by method (1a) was lower by one order of magnitude than in the previous instances at the same temp. The diffusion coeffs. in instances (1b), (2a), and (2b) were higher than in instance (1a) because the transfer of water was accelerated by capillary forces at the unsatd. boundary which was present between the satd. body and ambient atm. for (2a) and (2b) or between the satd. and unsatd. body for (1b).

97: 132191a **Petrography and mineralogy of clays in relation to quick kiln-burning processes.** Bastida Cuairan, Joaquin (Inst. Quim. Tec., Valencia, Spain). *Bol. Soc. Esp. Ceram. Vidrio* **1982,** 21(1), 15–22 (Span). The properties of clays which are typical of those in Catellon and the bordering regions of Valencia and Teruel were detd. and their relationship to rapid firing for manuf. of ceramic coatings and linings for footpaths was studied.

97: 132192b **The martensitic transformation. Its importance in the design of future ceramic materials.** Osendi, M. I.; Moya, J. S. (Inst. Ceram. Vidrio, Madrid, Spain). *Bol. Soc. Esp. Ceram. Vidrio* **1982,** 21(1), 33–9 (Span). Martensitic transformation was analyzed thermodynamically and crystallog. and studied in ZrO_2–based ceramics. Several previously studied materials are discussed and their highly increased toughness is attributed to the martensitic transformation effect.

97: 132193c **Crystallization of the glassy phase of grain boundaries in silicon nitride.** Jefferson, D. A.; Wen, Shulin; Thomas, J. M. (Dep. Phys. Chem., Univ. Cambridge, Cambridge, UK). *Guisuanyan Xuebao* **1982,** 10(1), 1–8 (Ch). Three Si_3N_4 ceramics contg. 5 Y_2O_3 and 2 wt.% Al_2O_3, which were subjected to different heat-treatments after hot-pressing, were examd. by x-ray microanal., x-ray diffraction, and high-resoln. electron microscopy. The results indicated that there were phase changes in the grain boundaries of the samples during heat-treatment, the glassy phase at the grain boundaries being crystd.

97: 132194d **Preparation of active powder for PLZT transparent ceramics by alcohol dehydration of citrate solutions.** Li, Chengen; Ni, Huanyao; Yin, Zhiwen (Shanghai Inst. Ceram., Acad. Sin., Shanghai, Peop. Rep. China). *Guisuanyan Xuebao* **1982,** 10(1), 9–16 (Ch). The prepn. of citrate solns. for ceramic powder synthesis using alc. dehydration, the dehydration treatments, and control of the chem. compn. were studied. Some technol. parameters for prepg. Pb La titanate zirconate ceramic powder by this method are proposed. The powders thus obtained have a compn. very close to the required formula, are extremely fine (mostly <0.2 μ), and after hot-pressing in O give good transparency and better chem. and optical homogeneity than that obtained by conventional oxide technol.

97: 132195e **Effect of doped zirconia on the mechanical behavior of Nasicon ($Na_3Zr_2Si_2PO_{12}$) ceramics.** Zhang, Qingchun; Lin, Suzhen (Shanghai Inst. Ceram., Acad. Sin., Shanghai, Peop. Rep. China). *Guisuanyan Xuebao* **1982,** 10(1), 17–24 (Ch). The strength data of Nasicon ($Na_3Zr_2Si_2PO_{12}$) ceramics as measured on ring specimens fitted well to the Weibull distribution with a modulus of 3.2. The mean strength of the ceramics was 107 MN/m^2, which is between the 3- and 4-point bending strengths, the former being 15% lower than the latter. The strength of $Na_3Zr_2Si_2PO_{12}$ ceramics varied as a reciprocal linear function of the sq. root of the length of Knoop's indentation, or equiv. of the square root of the grain size. The toughness parameter (K_{Ic}) of undoped Nasicon ceramics was 2.04 MN/m$^{3/2}$. It increased with ZrO_2 dopant addn. up to 3 mol%, but the strength changed rather insignificantly. As the content of ZrO_2 was increased further, both the strength and K_{Ic} decreased. When the ZrO_2 was increased to >5 mol%, the elec. resistivity began to increase from a value of ~3.5 Ω-cm. These results support the view point that the change of mech. properties results from the energy absorbing small matrix microcracks which are formed by the expansion of ZrO_2 during the tetragonal–monoclinic transformation. The applied stress may addnl. affect the phase transformation.

97: 132196f **Effect of metal oxide additives in small quantities on the microstructure and properties of alumina ceramics.** Fan, Fukang; Tian, Yuling (Nanjing Inst. Chem. Technol., Nanjing, Peop. Rep. China). *Guisuanyan Xuebao* **1982,** 10(1), 25–36 (Ch). The effects of oxide dopants on the microstructures and properties of Al_2O_3 ceramics, based on CaO–Al_2O_3–SiO_2 and MgO–Al_2O_3–SiO_2 systems were studied. Samples with higher mech. strength were characterized by an interceptive or mosaic structure. The addn. of 1% ZrO_2 or CeO_2 in the system CaO–Al_2O_3–SiO_2 was less effective in controlling the crystal growth of corundum in the L^3 direction in the system MgO–Al_2O_3–SiO_2. The crystal growth is anomalous in samples of either system doped with 1% CeO_2. The mech. strength depended not only on crystal grain-size, but also on the morphol. and the distribution of grains, compn. of the grain boundary, and porosity under certain conditions (crystal size >1 μ). An Al_2O_3 sample contg. MgO and 1% Ta_2O_5 had a marked decrease of sintering temp., increase of mech. strength, and improvement of elec. properties and chem. stability as compared with samples contg. CaO or MgO. The Al_2O_3–MgO–1%Ta_2O_5 sample was characterized by a euhedral equigranular texture, comprised of small short prismatic crystals of corundum.

97: 132197g **Effect of varying technological parameters and nickel(II) oxide doping on sintering of alumina ceramics.** Cui, Guowen; Coble, R. L. (Qinghua Univ., Beijing, Peop. Rep. China). *Guisuanyan Xuebao* **1982,** 10(1), 37–44 (Ch). Polycryst. Al_2O_3 ceramic samples were fabricated from Al_2O_3 XA-139 powders with varying amts. of NiO dopant by sintering in air or O. The temp., atm., and the amt. of NiO affected the prefiring and sintering ds. of the Al_2O_3 ceramics in different ways. A defect structure is proposed to explain the phenomena. The kinetics in the final stage of sintering and the role of NiO dopant in the densification of the Al_2O_3 ceramics are discussed. The fracture surface of the sample (d. 99.8%) was analyzed with a scanning Auger microprobe which confirmed that a solid soln. model is a possible mechanism.

97: 132198h **Zeta potential of ceramic materials. Parameters affecting its determination by the streaming-potential technique.** Volzone, C.; Pereira, E. (Cent. Tecnol. Recur. Miner. Ceram., 1897 Argent.). *An. Asoc. Quim. Argent.* **1982,** 70(3–4), 469–78 (Span). The steaming potential technique for the detn. of the ζ-potential of components of ceramic mixts. is affected by the particular parameters of the materials and of the operating conditions. The nature and degree of influence of such factors were studied. The following materials were used: kaolin, quartz, and feldspar in different particle sizes, and natural clay materials with interchangeable ions at different stabilization times of the system, i.e. the time elapsed between the introduction of the sample in the measuring system and the measurement of the property.

97: 132199j **Material and process technical relations in the manufacturing of ceramic films.** Nobst, Peter; Spauszus, Sigmar; Jung, Joerg (Wissenschaftsber. Silikattech., Hochsch. Archit. Bauwesen, Weimar, Ger. Dem. Rep.). *Silikattechnik* **1982,** 33(5), 137–40 (Ger). The prepn. of ceramic films by the doctor-blade process was reviewed and modeled and the individual process studied. Prepn. of the casting slip, the casting process, drying, and the processing properties of the ceramic film are discussed.

97: 132200c **Study of the composition of phases originating in the interaction of titanium-containing solders with alumina ceramics.** Bushkov, A. A.; Kozlovskii, L. V.; Kheifets, V. S. (Leningrad, USSR). *Adgez. Rasplavov Paika Mater.* **1981,** 8, 67–72 (Russ). X-ray diffraction, electron microprobe anal., and optical microscopy were used to study the chem. interaction of Al_2O_3 ceramics (22KhS) with Ti-Ni [12668-67-6] and Ti-Ni-Cu [80207-48-3] solders. The interface of the ceramics and Ti-Ni solder contained TiO_2 and $AlTi_2$ [12003-97-3] and that of the ceramics and Ti-Ni-Cu solder contained TiO_2, Ti_2Al, TiO, and $AlTi_3$ [12003-98-4]. The addn. of Cu to the Ti-Ni solder intensified the Ti-Al_2O_3 reactions and increased the strength of the soldered joint.

97: 132201d **Comments on "Fracture stress-reflecting spot relations in hot-pressed alumina".** Rice, R. W. (Nav. Res. Lab., Washington, DC 20375 USA). *J. Mater. Sci.* **1982,** 17(5), 1537–9 (Eng). A polemic. The variation and size of the stress intensity of the reflecting spot are obsd. on ceramic fracture surfaces are not inconsistent with this area being the inner mirror contrary to the statement by H. P. Kirchner and J. M. Richard (*ibid.* **1980** 15, 1319) that the variation is inconsistent with that conclusion.

97: 132202e **An internal friction study of elevated-temperature properties of sintered silicon nitrides as a composite.** Shioiri, J.; Satoh, K.; Fujisawa, Y. (Fac. Eng., Univ. Tokyo, Tokyo, Japan 113). *Commos. Mater.: Mech., Mech. Prop. Fabr., Jpn.-US Conf.* **1981,** 281–8 (Eng). Edited by Kawata, Kozo; Akasaka, Takashi. Jpn. Soc. Compos. Mater.: Tokyo, Japan. Temp. dependences of the rigidity and internal friction of hot press sintered (HPS), pressureless sintered (PLS), and reaction sintered (RS) Si_3N_4 were measured by the torsion

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氮化硅晶界玻璃相结晶化的研究*

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摘 要

三种经过不同温度下热处理的热压氮化硅样品（含5wt%Y_2O_3和2wt%Al_2O_3添加物），用X射线衍射、X射线微量分析和高分辨率电子显微镜进行了研究。结果表明在热处理后晶界区产生相变化。晶界玻璃相由于热处理而结晶化。

一、引 言

氮化硅是作为高温工程应用的一种最为重要的特种结构陶瓷材料，它有希望用于1300°C高温燃气透平，高于现有的任何高温合金[1,2]。

但是它的性能，特别是机械性能，在很大程度上决定于晶界相。目前使它不能在高温下应用的一个原因，是它的强度在1000°C以上有较大地下降[3,4]。

这种下降主要是由于晶粒间玻璃相的存在。当温度升高，玻璃相的粘度下降而产生流动，使晶粒与晶粒可以相互滑移[5]。

本工作的目的在于确定，当热处理使晶界玻璃相结晶时，在晶界所发生的相变化。

二、实 验 方 法

这项工作研究了三种Si_3N_4样品[6]。第一种是热压Si_3N_4，由α-Si_3N_4为主的粉末原料，添加5wt%Y_2O_3和2wt%Al_2O_3，在1750°C保温2h热压而成。

第二种试样是将第一种样品在1200°C热处理60h而得。第三种样品则是把第一种再在1400°C热处理60h而得。

为进行电子显微镜研究的样品，先用金刚石锯切割，并用超声钻从切片上钻下约0.2mm厚的圆片，在碳化硅砂纸上研磨加工，然后在金刚石砂纸上磨到厚度约20μm，最后用氩离子束将样品减薄到对电子显微镜透明。氩离子束对样品表面的入射角为20°。

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** 此项工作是和我所陈绮桃、严东生等合作进行。作者感谢英国皇家学会和中国科学院对科学交换项目的支持。
*** N. W. Jepps帮助制备样品；K. Liddell和P. Korgul协助X射线和电子显微镜工作，与K.H.Jack和D. P. Thompson进行有益的讨论，特此一并致谢。

进行X射线粉末衍射研究的样品，磨到细度通过300mesh，采用*Hägg—Guinier*聚焦照相机。用块状试样进行X射线衍射试验，采用*Philips* X射线衍射仪。

作为透射电子显微镜研究（TEM）及微区分析的样品，可用粉碎的Si_3N_4碎片，或用上述方法减薄的薄片样品。TEM与微区分析研究是在*Philips EM*300上进行，它附有透射扫描（STEM）与X射线能量散射（EDX）附件。

高分辨率电子显微镜照片与晶格象是在*JEOL*200*CX*上摄取，它的分辨率（线—线）达到1.4Å。

三、实 验 结 果

三种试样的X射线衍射图案都表明只有一种主晶相，即β'-Si_3N_4和四种微量次晶相（即WSi_2、WC、α-W_2C及微量的α-Si_3N_4），其中可以认为WSi_2是从WC按以下反应而成：

$$3WC+2SiO_2=WSi_2+W_2C+2CO_2$$

以上的五种晶相，经过热处理后，也不发生变化。但是其余的次要晶相，主要是含钇的相，在热处理时则发生相变化，见图1(1)、(2)。

所得结果列于下表：

晶相**	热压样品	1200°C热处理60h	1400°C热处理60h
β'-Si_3N_4 六方 $a'=7.606$ $c'=2.909$	主量	主量	主量
α-Si_3N_4 六方 $a=7.758$ $c=5.623$	微量	微量	微量
WSi_2 四方 $a=3.211$ $c=7.868$	微量	微量	微量
WC 六方 $a=2.906$ $c=2.838$	微量	微量	微量
α-W_2C 六方 $a=2.99$ $c=4.71$	微量	微量	微量
Y、N硅灰石，$YSiO_2N$ 六方 $a=7.01$ $c=9.10$	微量	—	—
*Y_2SiO_5，单斜 $a=10.34$，$b=6.689$ $c=12.38$，$\beta=102.5°$	微量	微量	—
Y、N磷灰石，*H*相，$Y_5(SiO_4)_3N$ 六方 $a=9.42$，$c=6.76$	—	微量	微量
Y、N黄长石，$Y_2Si_3O_3N_4$ 四方 $a=7.597$，$c=4.908$	—	—	微量

* 在部分样品中观察到。

** 晶胞尺寸单位Å。

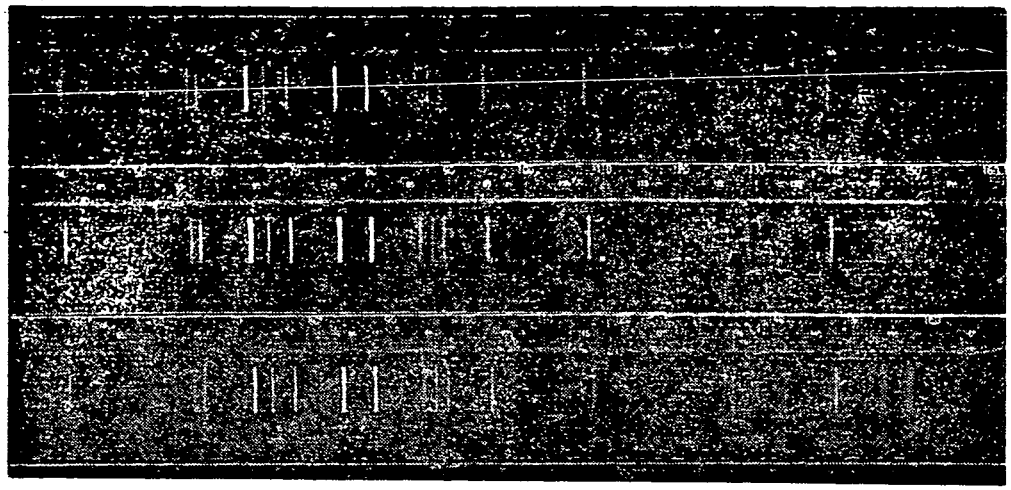

图 1(1) 粉末样品X射线衍射谱

图谱表明大部分未处理样品的晶界所含Y相为$YSiO_2N$；1200℃热处理样品为H相；1400℃样品为H相和$Y_2Si_3O_3N_4$黄长石相(见表)

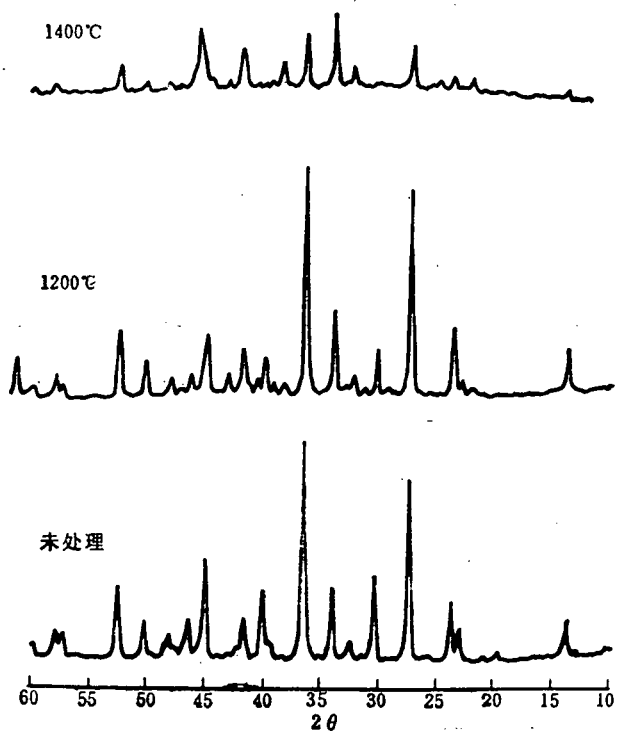

图 1(2) 块状样品X射线衍射图谱

给出结果与图1(1)的照片相同，但在未处理和经1200℃处理的某些样品中发现有微量Y_2SiO_5

上表所列的结果表明，为了改善决定着机械性能的晶界相，主要是含Y的相，热处理是一种办法，同时也并不对主晶相有什么影响。

1.晶粒形貌

所有样品的显微结构都包含着一种主要的晶相（即β'-Si_3N_4），和两类次晶相或称微量相。

第一类微量相通常在多晶粒交界处可以看到（见图2），但有时也可在较大的区域内发现，这时微量相部分地、甚至全部地包围着β'-Si_3N_4晶粒（图2，区域2）。

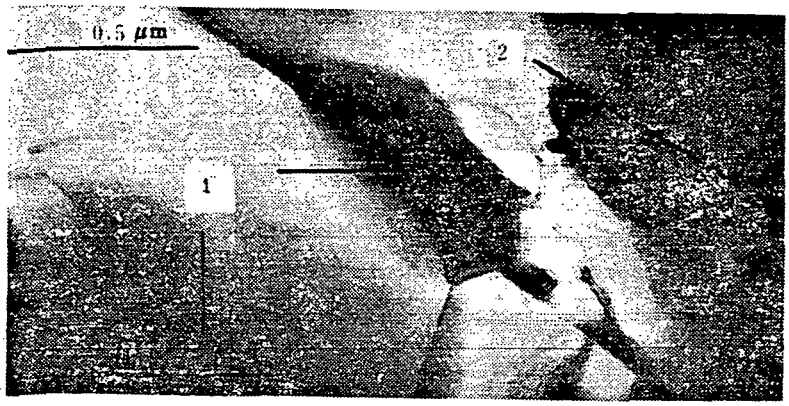

图 2 主晶相和次晶相(微量相)

区域1—多晶粒的交界；区域2—微量相部分地或全部包围着β'-Si_3N_4晶粒

电镜微量分析表明，这种区域比其它区域有更多的杂质，如Ca、Mg、Fe、Cr、Ni、Ti、Cu等（图3），它们显然来自原料。电子衍射图指出，这种地方和其它区域相比，存在着更多的玻璃相，并从衍射环的强度判断，经过热处理的样品，其玻璃相含量远比未处理的样品为少。

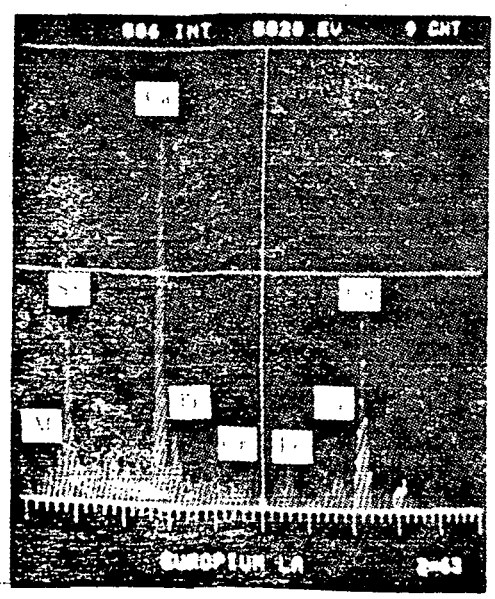

图 3

能谱分析电子显微镜，用*Philips EM*300附能量散射谱仪(EDX)，结果表明在图2区域2有更多的杂质

第一类微量相包括加工时引入的杂质WC、WSi_2、W_2C，它们通常是球形的、不透明的颗粒（图4）；也包括含Y的相，除玻璃态外，还有不少含Y、N的晶相，如Y_2SiO_5、α硅灰石、H相和黄长石（图4、5），它们的出现决定于热处理温度（见表）。

第二类微量相只在两晶粒间界上出现，通常呈玻璃相，但可晶化为晶相。

主晶相β'-Si_3N_4有些具有近似等轴晶形，晶粒尺寸约在0.3～1.2μm范围内。有些晶粒的截面呈六方长柱状，长/宽比可达3～4，但多数是棱柱状，长/宽比在1～2之间。统计地说，经过热处理样品的晶粒尺寸比未经过热处理者稍大（图4、5）。

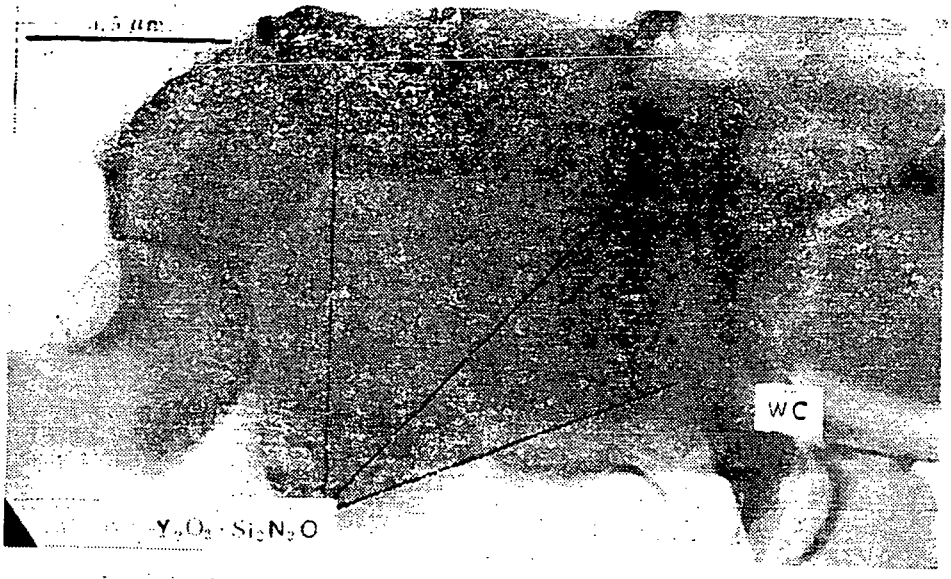

图 4

在未处理的氮化硅样品中，$YSiO_2N$相的分布

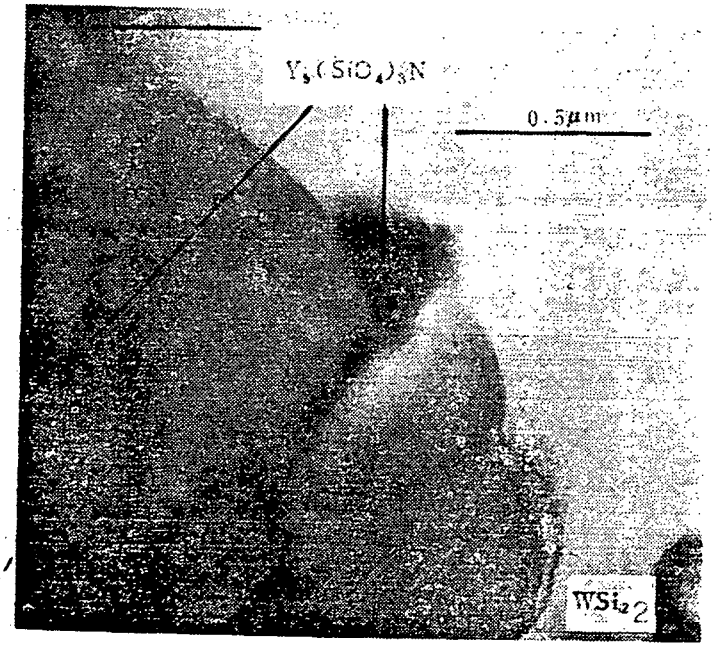

图 5

在经1200℃热处理样品中，$Y_5(SiO_4)_3N$相的分布

β'-Si_3N_4含（100）晶面的晶格象示于图7。可以看到在晶粒的左边有若干台阶，显示着在热压时晶粒长大的象征。

从上表可见β-Si_3N_4的晶胞参数a'值比β-Si_3N_4的a值稍大。表明少量Al_2O_3进入β-

Si_3N_4晶格形成β'-Si_3N_4固溶体，但多数Al_2O_3分散于晶界的玻璃相中。

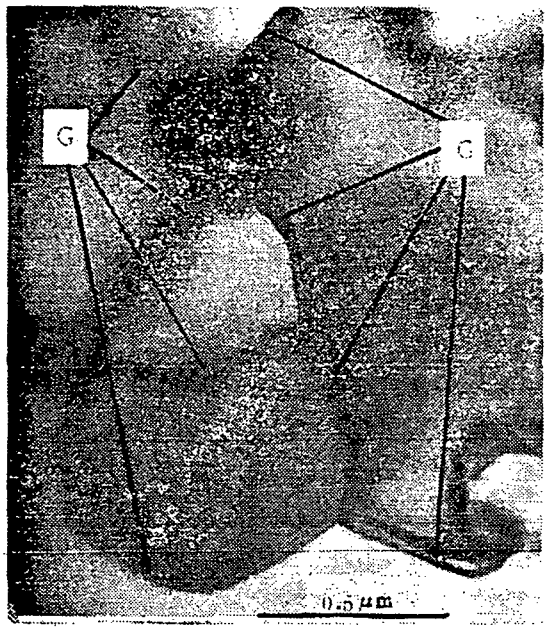

图 6
未处理的氮化硅样品的明场照片，显示出在晶界周围的玻璃相

2.晶界相

所有的含Y相都是微量相。从样品的新鲜表面进行的分析结果表明，Y没有进入到氮化硅的晶格中去。

第一类的微量相，既有结晶相，也有玻璃相。那些结晶相的组成已在上表中列出；但是玻璃相的成分，则不同区域有很大的差异。玻璃相的存在可用衍射图案、明场和晶格像等方法来进行鉴定。图4、图5是明场显微照像，显示出晶粒间的玻璃相。如果采用倾斜技术，使晶界与电子束平行[7]，则在晶界处都可以看到玻璃相的存在（图6）。

采用衍射图案方法，可以确定未经处理的样品比在1200°C或1400°C处理过的样品含有更多的玻璃相。用明场及暗场技术，对第一类微量相可以得到较好的结果。至于第二类微量相，常常难于简单地肯定它们在热处理后是否结晶化了，但是本工作仍旧得到了一些结果（图8）。

图8（1）是两个β'-Si_3N_4晶粒的晶格像和在它们之间的晶界。选择区域衍射图[图8（2）]、高分辨率暗场像[图8（3）]和高分辨率明场像[图8（1）]的结果都表明，经过1400°C热处理后，晶界区是结晶化了。

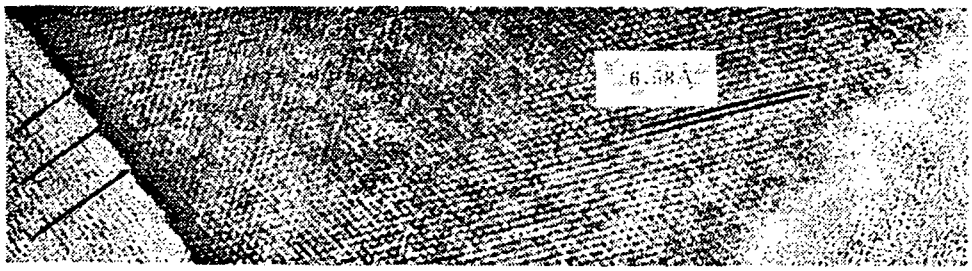

图 7 β'-Si_3N_4含(100)晶面的晶格像
晶粒左边表面的台阶显示热压时氮化硅晶粒的生长

获得晶界与电子束平行的条件后[8]，仍需要很长时间才得到这样适当的晶格像。假如试样台达到的倾斜角度不够，常常不能鉴定或判断在晶界的第二类微量相是否结晶化了。这是因为第二类微量相的区域（晶界区）的宽度常常只有30Å(图8)，有的甚至薄到约6Å(图9)。

图10是β'-Si_3N_4三晶粒的晶格像以及它们之间的晶界。通常在这类的晶界区有更多的

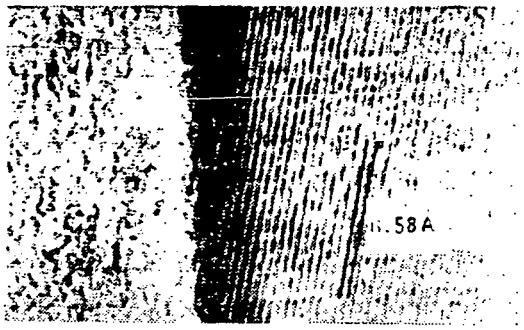

图 8(1) β'-Si_3N_4两晶粒及晶界的晶格像

用50μm物镜孔径拍摄。试样在1400°C经长时间热处理

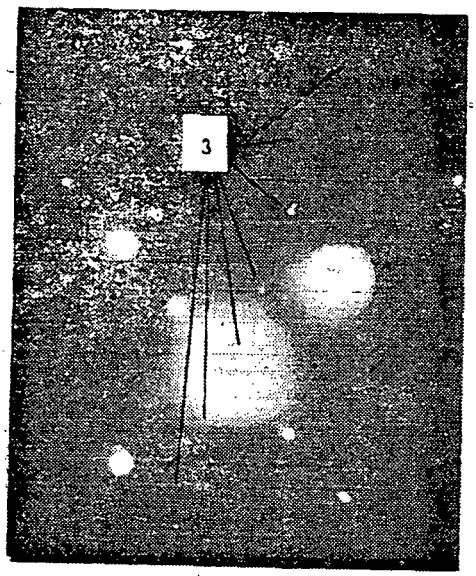

图 8(2) β'-Si_3N_4两晶粒及晶界区域的选择区域衍射(SAD)图案

表明晶界与电子束呈平行的方向出现第三套衍射斑点

图 8(3) 样品同一区域的高分辨率暗场照片

在晶界处显示出晶格像

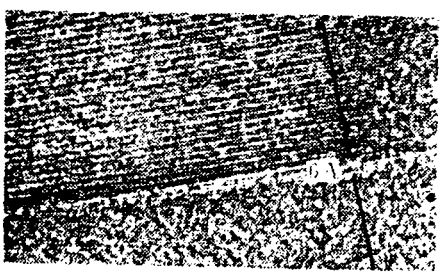

图 9 未处理Si_3N_4样品的晶格像和晶界

表明沿着晶粒晶界的厚度是变化的，最小厚度约6Å

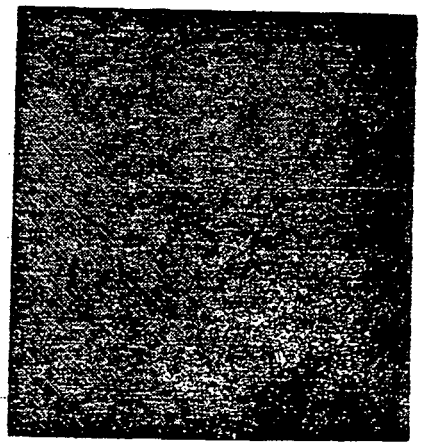

图 10 经1200°C热处理样品中三晶粒的晶格像和它们的晶界

玻璃态存在。

四、讨 论

以上的结果表明，当比热压低一些的温度热处理，如1200°C和1400°C时，可以使在晶界的部分玻璃相结晶化。由于样品并不是很均匀的，尤其在高分辨率电子显微镜的尺度下，需要做大量的试样工作，才能给出统计性的结果。本文所有照片都是带有典型性的。

按照Tsuge[9]的观点，对Si_3N_4-SiO_2-Y_2O_3系统加入少量Al_2O_3，可使晶粒间更容易形成玻璃相。在我们所研究的样品中，不论用X射线或电子衍射方法，都没有发现石榴石相。β'-Si_3N_4固溶体的晶胞参数和β-Si_3N_4甚为接近，表明大部分Al_2O_3存在于玻璃相之中。

Quackenbush等[10]指出Al_2O_3溶于晶界相中将阻碍结晶化，从而促进玻璃相的形成。本工作的结果表明，尚没有发现含Al的晶相，即使热压材料经过热处理后也是如此。

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A STUDY OF CRYSTALLIZING GLASSY PHASE OF GRAIN BOUNDARY IN SILICON NITRIDE

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Abstract

Three silicon nitrides(with 5 wt% Y_2O_3, 2 wt% Al_2O_3 additives), which were subjected to different temperature thermo-treatment after hot-pressing, were examined by X-ray microanalysis, X-ray diffraction and high resolution electron microscopy. The results showed that there were phase changes in grain boundaries of the samples during thermo-treatment, and the glassy phase at the grain boundaries was crystallized by thermo-treatment.