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Microstructure observation of β-sialon-15R ceramics synthesized from aluminum dross

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Abstract

Fully dense β-sialon-15R multiphase ceramics were synthesized by hot pressing sintering using aluminum dross as raw material. Transmission electron microscopy (TEM) was used to study the microstructure, notably for the impurity and glass phase. The results show that β-sialon grains are generally equiaxed, and 15R AlN polytypoid grains show a fibre-like morphology. The main impurity phase is Fe_5Si_3. High resolution electron microscopy (HREM) results confirm the interface between β-sialon grains and/or 15R grains to be clean in the sample synthesized at 1750 °C, and the glassy phase only exist in triple junctions and pockets. AlN polytypoids in the multiphase ceramics provide a path to reduce the glass phase formed from the oxide impurity in aluminum dross.

Keywords: A. Hot pressing; B. Microstructure-nal; D. Sialon; Aluminum dross

1. Introduction

Sialon ceramics are promising candidates for engineering applications because of their excellent mechanical, chemical, and thermal properties [1]. However, the applications of sialon ceramics have always been limited by the high cost for the use of high-purity raw materials. Then many works were devoted to synthesize sialon using low cost raw materials, including kaolinite, clay, bauxite, and industrial wastes such as fly ash, slag, etc. [2–6]. In almost all cases, the researches mainly focused on the effects of initial material and reaction parameters on the synthesis of sialon powders, and dense sialon ceramics were seldom fabricated. To date, although impurity is an important aspect to utilize industrial wastes, little study has been done on the situation of impurity in the final materials.

Aluminum dross is one of the main secondary wastes during aluminum recycling procedure [7]. The earlier research indicated that a large amount of metallic Al in aluminum dross should have the potential not only to work as a reducing agent but also to synthesize AlN polytypoid, which can be introduced into sialon ceramics as a toughening phase [8–11]. In addition, another advantage of using AlN polytypoid as a main component is that AlN polytypoids have mostly glass-free interfaces in multiphase ceramics [12]. Hence it is proposed that β-sialon-AlN-polytypoid multiphase ceramic can be synthesized from aluminum dross.

The effects of initial composition and sintering parameters on the formation of β-sialon-AlN-polytypoid ceramic by pressureless sintering of aluminum dross were previously investigated by the present authors, but the sialon materials formed were found to exhibit low density [8]. In order to clearly identify the situation of impurity and glass phase in the final materials, it is necessary to investigate the microstructure of dense sialon ceramics using TEM method. In present work, fully dense β-sialon-15R multiphase ceramics are prepared by hot pressing sintering using aluminum dross, and the microstructure and particularly the situation of impurity and glass phase are analyzed in detail by TEM and related methods.

2. Experimental

The aluminum dross (320 mesh) used in this work is provided by the aluminum recycling company Shanghai Sigma

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Metals Inc. The main chemical contents are Al (31.8%, in mass, the same as following), Al_2O_3 (25.1%), SiO_2 (9.9%), CaO (3.6%), MgO (9.7%), Fe_2O_3 (4.8%) and some other impurities such as NaCl, KCl, etc. Silicon powder (99%, 200 mesh) used as a reducing agent and Si_3N_4 powder (96%, 320 mesh) added as seed are commercial products [13]. We have reported that [8] the optimal initial composition is D2 to synthesize sialon using aluminum dross, and D2 composed of 58% aluminum dross, 39% Silicon and 3% Si_3N_4 is designed as the initial composition in this paper. The raw powders are mixed by ball milling with silicon nitride medium in absolute alcohol for 12 h and then the dry mixed powders are sintered by hot pressing in a nitrogen atmosphere for 4 h under a pressure of 15 MPa, at 1650 °C and 1750 °C, respectively. The phase constitution is identified by powder X-ray diffraction (XRD, D/MAX 2550VL/PC) analysis with nickel-filtered Cu Kα radiation. Specimens for TEM studies are prepared by cutting thin sections from the hot pressing discs. A thin section is then mechanically polished to a thickness less than 30 μm followed by ion milling until the specimen is perforated. Finally, the ultra-thin plate is sputtered with amorphous carbon to the thickness of about several decades of nanometers. The specimens are then analyzed by a transmission electron microscope (JEM 2100F, JEOL).

3. Results and discussion

3.1. Phases and microstructures

The phase compositions of the samples synthesized at 1650 °C and 1750 °C (hereafter, named Sample-1650 and Sample-1750) are shown in Fig. 1. The main phases of two samples are β-sialon and 15R, and Fe_5Si_3 as the main impurity is found. Compared the relative intensities of the peaks located from 30° to 35° in Fig. 1, the trend of transformation of 15R to β-sialon from 1650 °C to 1750 °C can be clearly found. With the higher sintering temperature, more liquid phase occurred in sintering process. The liquid phase is oxygen-rich which could facilitate the formation of β-sialon. Fig. 2(a) shows a typical microstructure of the Sample-1750. β-Sialon grains are generally equiaxed, and 15R grains present a fibre-like morphology. The in situ growth of fibre-like 15R is expected to enhance the fracture toughness of sialon multiphase ceramics. The selected area electron diffraction (SAED) patterns of β-sialon and 15R are shown in Fig. 2(b) and (c), respectively. A little amorphous glassy phase is concentrated mainly in the pockets formed between the β-sialon grains and 15R grains. Fig. 3 shows a typical morphology and electron diffraction pattern of Fe_5Si_3. Impurity phase and sialon phase can be clearly identified by their different contrast. It is believed that Fe can react with Si to generate Fe_xSi_y [14]. Therefore, the impurity Fe from aluminum dross is retained at the final product in the form of Fe_5Si_3.

A special phenomenon should be focused from the inset area in Fig. 2(a). When the β-sialon grain is in contact with a 15R grain, its sharp faceted cross section is always found to smooth out, and the β-sialon grain can cut into and fit with the 15R grain. Previous work on β-sialon-12H multiphase ceramics found a mosaic structure of β-sialon and 12H grains [10], and this mosaic structure between β-sialon and 15R is also discovered in the present work and seems to widely exist in the β-sialon-AlN-polytypoid multiphase ceramics. Wang et al. [10] speculated that it might be the general process of solution–diffusion–nucleation–reprecipitation displays. When a β-sialon crystal gets in touch with one or a few AlN polytypoid crystals, its growth kinetics differs from a free-standing mode. Some material transport probably occurs between β-sialon and AlN polytypoid phase or maybe even through the grain boundary among them, which can be used to explain the intergrowth of

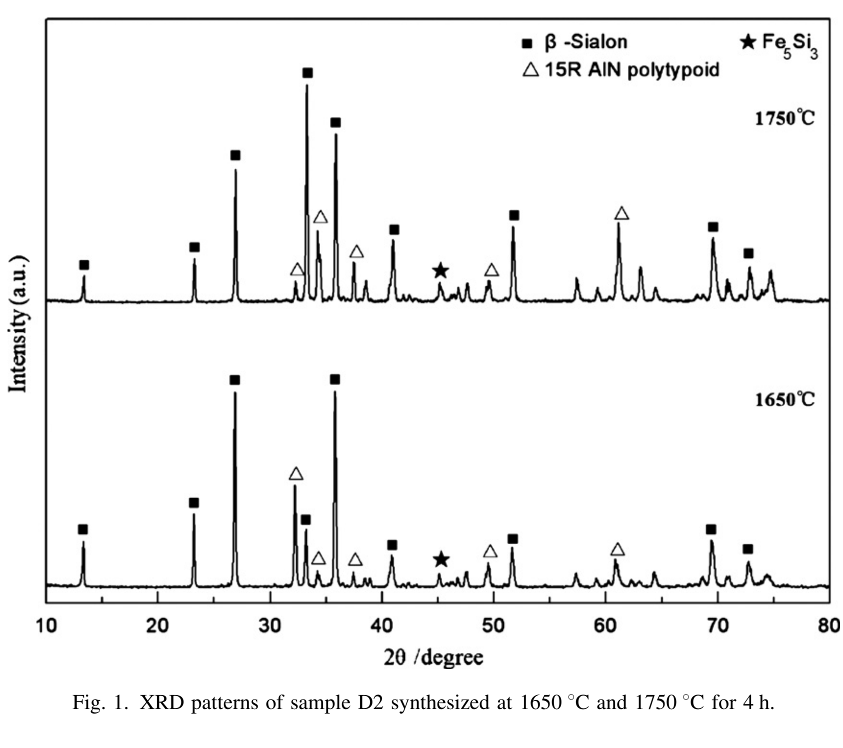

Fig. 1. XRD patterns of sample D2 synthesized at 1650 °C and 1750 °C for 4 h.

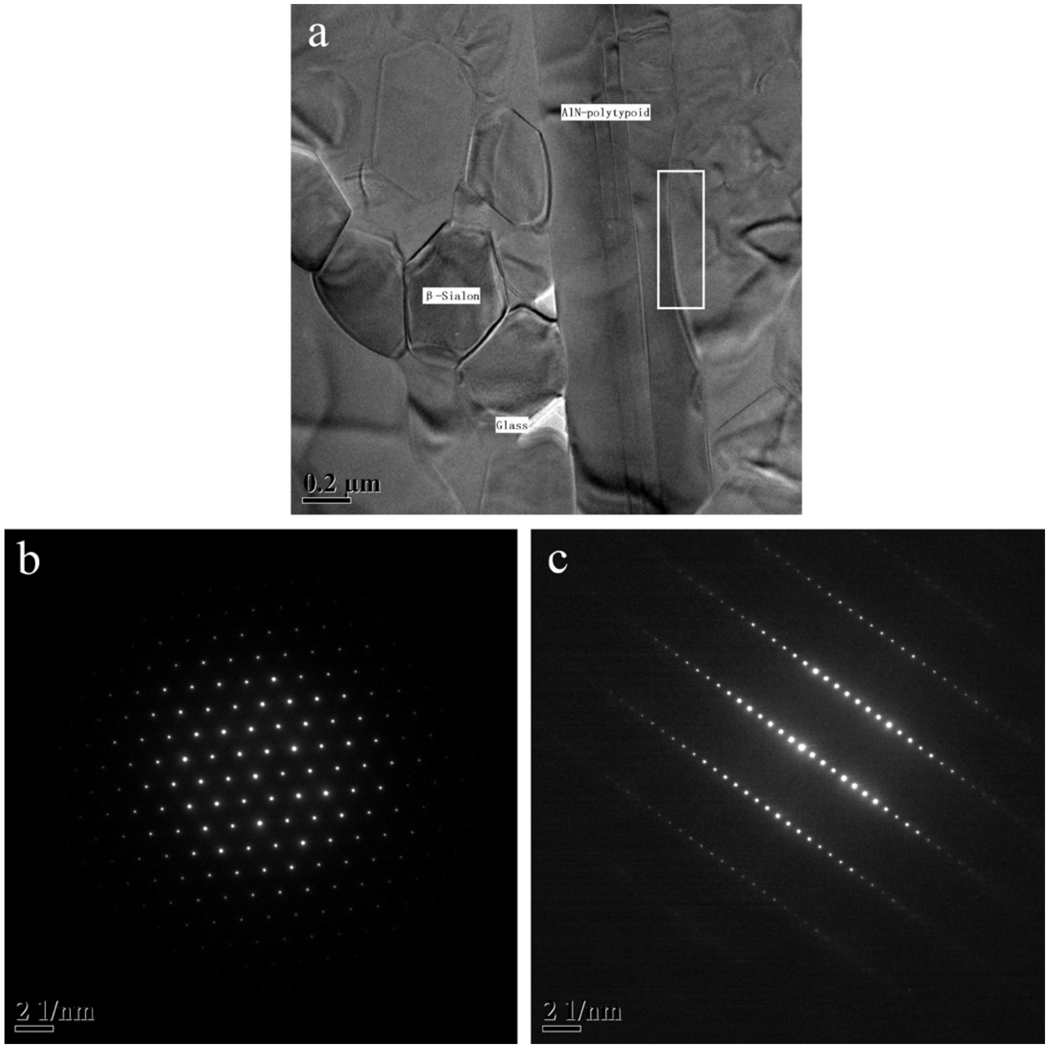

Fig. 2. (a) TEM micrograph of the β-sialon-15R ceramics synthesized at 1750 °C for 4 h. (b) SAED patterns of β-sialon. (c) SAED patterns of 15R.

AlN polytypoid and β-sialon grains and the change of β-sialon grain morphology. It is noticeable that this special microstructure can be expected to improve the mechanical properties of β-sialon-AlN-polytypoid multiphase materials.

3.2. Grain interfaces and triple-grain junctions

The main obstacle for utilizing industrial wastes to synthesize sialon is the high content of oxides in raw materials,

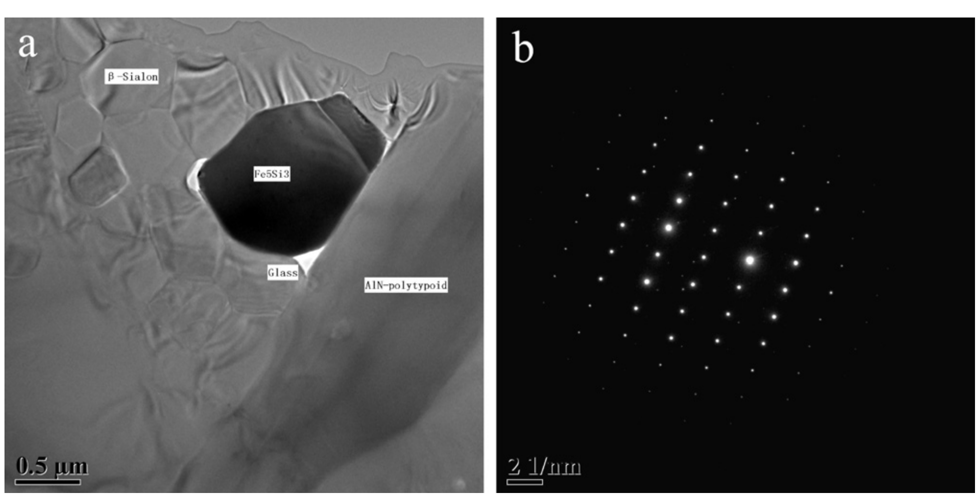

Fig. 3. A typical morphology (a) and SAED pattern (b) for Fe_5Si_3.

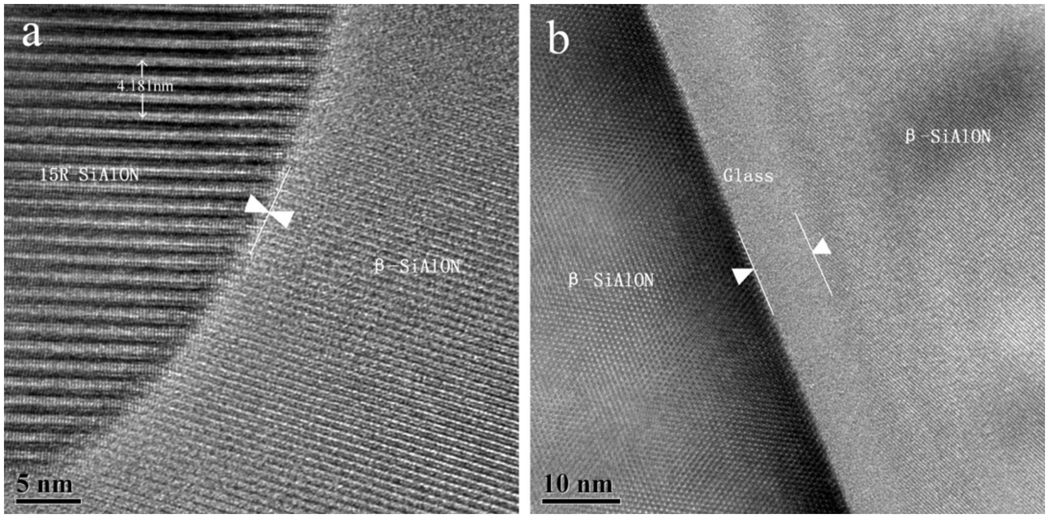

Fig. 4. HREM micrographs of the β-sialon-15R ceramics synthesized at 1650 °C.

which is inclined to form glassy phases at grain boundary thus deteriorating the mechanical properties. The present studies indicate that the preparation approach for β-sialon-15R is to control the residual liquid content, which has been remarkably successful in producing a nearly glass-free ceramic. Although the sintering mechanism remains that of solution-reprecipitation, the liquid is transient and its components are largely removed by the solid solution so that grain boundaries have no

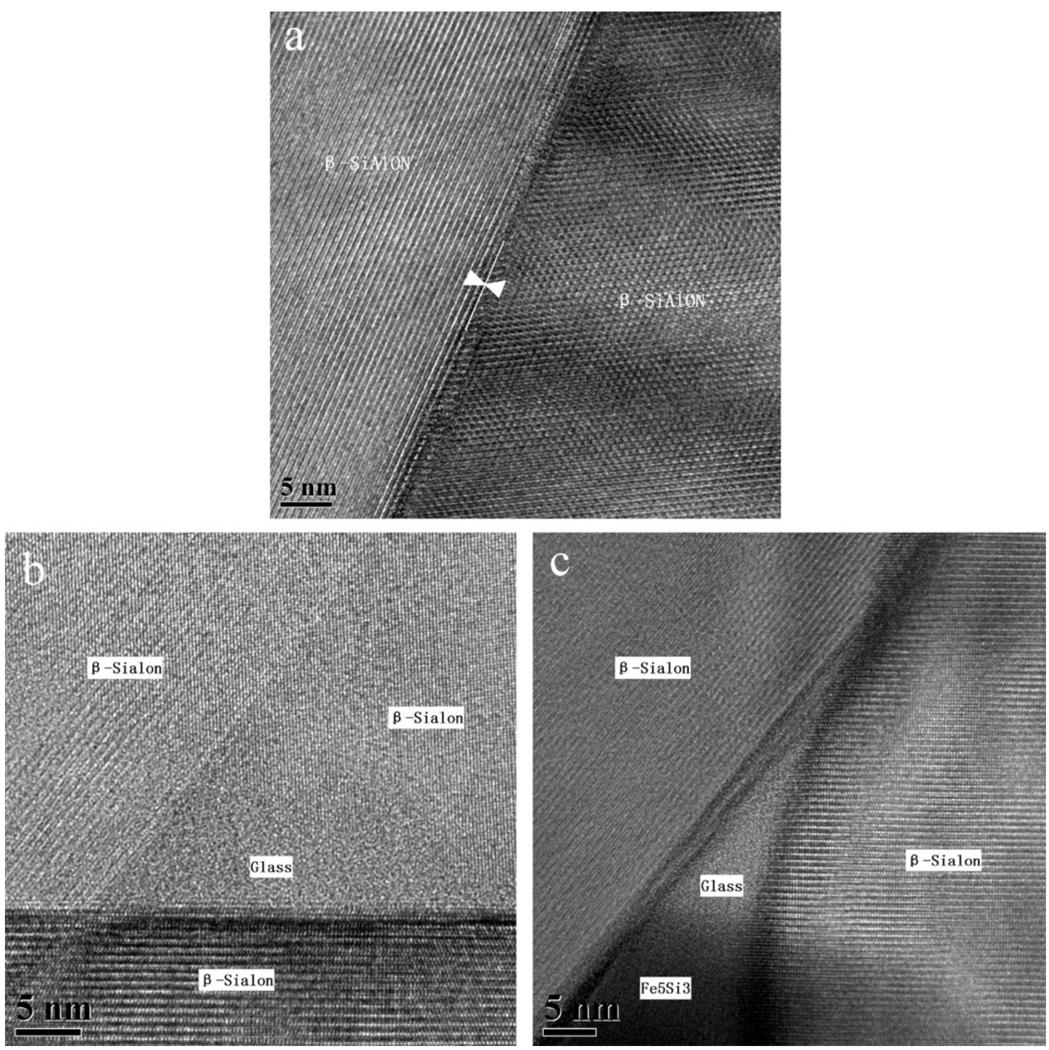

Fig. 5. HREM micrographs of the β-sialon-15R ceramics synthesized at 1750 °C.

obvious glass phase. Nevertheless, glassy phases may still be retained especially at triple junctions, but these may be isolated and fewer. To a certain degree, it is proved that AlN polytypoids in the multiphase ceramics offer an effective path to reduce the glass phase formed from the oxide impurity in aluminum dross.

High-resolution TEM images are used to detect any glassy phases present in grain boundaries. Fig. 4 shows the high-resolution TEM image of the Sample-1650. A grain boundary between β-sialon and 15R is shown in Fig. 4(a), and it is clear that no intergranular glassy phases are detected. The 15R grain is observed along the [1 0 0] zone. The lattice constant of the 15R phase in the c axis is 4.181 nm, consisting of three blocks with five layers each. A grain boundary between two β-sialon grains is presented in Fig. 4(b). It can be seen that the liquid phase penetrated into the grain boundary with a width of about 5 nm. Lattice coincidence does not exist in such β–β grain boundaries. However, one attraction is that various grain boundaries of the Sample-1750 (shown in Fig. 5), such as β–β and β-15R, are also observed, but no intergranular glassy phases are detected. From Fig. 5(a), it can be seen that the β–β grain boundary is clean. The glassy phase only exists in the triple junctions and pockets, as can be seen from Fig. 5(b) and (c). Statistically, one cannot exclude the existence of intergranular glassy phases in this ceramics, however, HREM examination of several interphase interfaces and triple junctions suggests that the amount of glassy phase may be decreased in the Sample-1750. It is suggested that the nearly glass-free sialon ceramics can be obtained from aluminum dross by choosing the right material compositional design and proper sintering parameters.

3.3. Impurity analysis

The impurity is usually another main obstacle to utilize industrial wastes. EDS results shown in Fig. 6 indicate that β-sialon grains is free of impurity, no metal cations enter. However, most of Mg cations from aluminum dross are incorporated into the AlN polytypoid and the content of Mg cations in 15R reaches 4.4%. It is believed that AlN polytypoid, having the capacity for incorporating a variety of metal ions into the interstices of the structure, will afford the possibility of making multiphase ceramics of much lower glass content. The study of Wang et al. [15] on (Ca and Mg)-α-sialon also indicated that the formation of magnesium containing AlN-polytypoid phase in the composite materials can provide a new approach to reduce the amount of glassy phase at the grain boundary. As explained above AlN polytypoids in sialon multiphase ceramics offer an effective path to reduce the glass phase formed from the oxide impurity in aluminum dross.

The EDS analysis of Fe_5Si_3 indicates some impurity elements such as Cr and Mn can be found in Fe_5Si_3 phase. The glassy phase is an oxygen-rich phase with the absence of obvious impurity. Some other impurities such as NaCl and KCl from aluminum dross are not found in sialon ceramics. This is

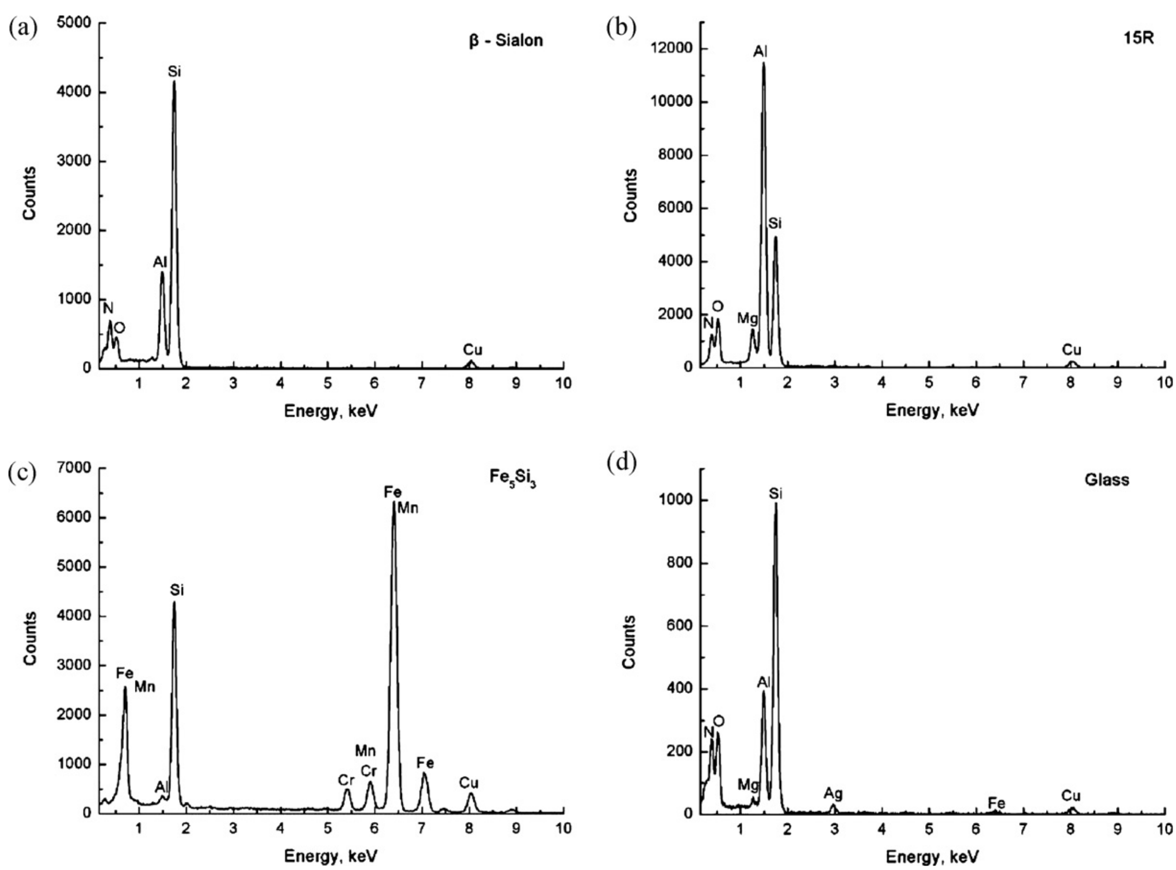

Fig. 6. EDS of the β-sialon-15R ceramics synthesized at 1750 °C.

because that the melting point of salts is about 1450 °C, and the salts impurities are evaporated from the samples during the sintering process. So, in the final products, the main impurity phase is Fe_5Si_3, and some minor elements impurity such as Cr and Mn is contained in Fe_5Si_3 phase.

4. Conclusions

Fully dense β-sialon-15R multiphase ceramics are successfully prepared by hot pressing sintering using aluminum dross. β-sialon grains are generally equiaxed and 15R grains show a fibre-like morphology. The main impurity phase is Fe_5Si_3. The interface between β-sialon grains and/or 15R grains is clean in the sample synthesized at 1750 °C, and the glassy phase only exist in triple junctions and pockets. β-sialon and 15R grains are free of impurity, and Fe_5Si_3 phase contains a noticeable amount of Cr and Mn. The glassy phase is an oxygen-rich phase with the absence of obvious impurity. AlN-polytypoids in the multiphase ceramics offer a path to reduce the glass phase formed from the oxide impurity in aluminum dross.

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References

[1] K.H. Jack, Sialons and related nitrogen ceramics – review, J. Mater. Sci. 11 (1976) 1135–1158.
[2] G. Lee, I.B. Cutler, Sinterable sialon powder by reaction of clay with carbon and nitrogen, Am. Ceram. Soc. Bull. 58 (1979) 869–871.
[3] J.Y. Qiu, J. Tatami, C. Zhang, K. Komeya, T. Meguro, Y.B. Cheng, Influence of starting material composition and carbon content on the preparation of Mg-α sialon powders by carbothermal reduction–nitridation, J. Eur. Ceram. Soc. 22 (2002) 2989–2996.
[4] W.W. Chen, P.L. Wang, D.Y. Chen, B.L. Zhang, J.X. Jiang, Y.B. Cheng, D.S. Yan, Synthesis of (Ca, Mg)-α-sialon from slag by self-propagating high-temperature synthesis, J. Mater. Chem. 12 (2002) 1199–1202.
[5] Q. Qiu, V. Hlavacek, S. Prochazka, Carbonitridation of fly ash. I. Synthesis of sialon-based materials, Ind. Eng. Chem. Res. 44 (2005) 2469–2476.
[6] T. Jiang, X.X. Xue, P.N. Duan, X. Liu, S.H. Zhang, R. Liu, Carbothermal reduction–nitridation of titania-bearing blast furnace slag, Ceram. Int. 34 (2008) 1643–1651.
[7] M.C. Shinzato, R. Hypolito, Solid waste from aluminum recycling process: characterization and reuse of its economically valuable constituents, Waste Manage. 25 (2005) 37–46.
[8] J.J. Li, J. Wang, H.Y. Chen, B.D. Sun, J.B. Jia, Synthesis of β-sialon-AlN-polytypoid ceramics from aluminum dross, Mater. Trans. 51 (2010) 844–848.
[9] W.W. Chen, Y.W. Li, W.Y. Sun, D.S. Yan, Phase formation and microstructural evolution of R-α′-AlN-polytypoid ceramics (*R* = *Y*, *Y* + Sm and Sm), J. Eur. Ceram. Soc. 20 (2000) 1327–1331.
[10] H. Wang, W.Y. Sun, H.R. Zhuang, J.W. Feng, T.S. YEN, Microstructural observation of β′-sialon-12H multiphase ceramics by HREM, Mater. Lett. 17 (1993) 131–136.
[11] P.L. Wang, W.Y. Sun, D.S. Yan, Mechanical properties of AlN-polytypoids – 15R, 12H and 21R, Mater. Sci. Eng. A 272 (1999) 351–356.
[12] C.S. Lee, X.F. Zhang, G. Thomas, Novel joining of dissimilar ceramics in the Si_3N_4–Al_2O_3 system using polytypoid functional gradients, Acta Mater. 49 (2001) 3775–3780.
[13] C. Zhang, K. Komeya, J. Tatami, T. Meguro, Y.B. Cheng, Synthesis of Mg-α sialon powders from talc and halloysite clay minerals, J. Eur. Ceram. Soc. 20 (2000) 1809–1814.
[14] S.M. Boyer, A.J. Moulson, A mechanism for the nitridation of Fe-contaminated silicon, J. Mater. Sci. 13 (1978) 1637–1646.
[15] P.L. Wang, C. Zhang, Y.X. Jia, W.Y. Sun, Densification, formation behavior and microstructure of (Ca, Mg)-α-sialon, J. Inorg. Mater. 14 (1999) 563–568.