Accepted Manuscript

The equilibria of Ta-W-Al-Si-O system at 1200 °C

Hongye Wang, Yuhong Chen, Zhangjun Bai, Baojun Zhao, Kang Wang, Laner Wu

PII: S0925-8388(17)34165-8

DOI: 10.1016/j.jallcom.2017.11.383

Reference: JALCOM 44076

To appear in: *Journal of Alloys and Compounds*

Received Date: 1 September 2017

Revised Date: 27 November 2017

Accepted Date: 30 November 2017

Please cite this article as: H. Wang, Y. Chen, Z. Bai, B. Zhao, K. Wang, L. Wu, The equilibria of Ta-W-Al-Si-O system at 1200 °C, *Journal of Alloys and Compounds* (2018), doi: 10.1016/j.jallcom.2017.11.383.

The equilibria of Ta-W-Al-Si-O system at 1200 ºC

Hongye Wang[1], Yuhong Chen[*], Zhangjun Bai[2], Baojun Zhao[3], Kang Wang[1], Laner Wu[1]

1. North Minzu university, Yinchuan, Ningxia 750021, China

2. CNMC Ningxia orient group Co.L.td, Shizuishan, Ningxia 753000 ,China

3. The University of Queensland, Brisbane, Queensland 4072, Australia

Abstract: Solid reactions among Ta-W-Al-Si oxides are discussed and the phase compatibilities of these oxides at 1200 ºC have been investigated. The results showed that complex oxides of $Ta_{22}W_4O_{67}$, Ta_2WO_8, $Ta_{16}W_{18}O_{94}$, $Al_2W_3O_{12}$ and $AlTaO_4$ could be formed by solid reactions. Liquid phase formed by Al_2O_3-WO_3 in WO_3-SiO_2-Al_2O_3 benefits the mullitization reaction, thus mullite can be formed at 1200 ºC in ternary system. Solid solution with a formula of $(1\text{-}x)Ta_2O_5 \cdot xWO_3$ was formed, and up to 25.0% SiO_2 and 6.0% Al_2O_3 can be dissolved in the solid solution. Liquid phase first appeared in the Ta_2O_3-WO_3-Al_2O_3 ternary system at 1300 ºC in the WO_3-rich corner. As the temperature increased, the liquidus area expanded towards the Al_2O_3- and the Ta_2O_5-rich corners.

Key words: Tantalum oxide; Tungsten trioxide; solid reaction; compatibility; solid solution; Liquidus boundary.

1.Introduction：

In recent years, advanced structural materials have been strongly required for application at temperature of above the maximum operating temperature of conventional high temperature engineering materials. Tantalum (Ta) and tungsten (W) have very high melting point (Ta: 3233K, W: 3693K), good erosion resistance, high strength and elastic modulus which are considered as excellent refractory metals in aerospace industry [1-3]. Due to the poor oxidation resistance of Ta, W and their alloys is still poor to be a barrier for their further application [4-6]. Smaller ionic radius, such as V, Al, Cu and Si, reduces the volume ratio of the oxides, thus alleviates spalling of the oxidation products from the surface [7]. Nowadays, a large number of alloying elements atnear-equimolar concentration have been used to form solid solution body-centered-cubic (bcc) or face-centered-cubic (fcc) phase crystal structure based on tantalum and tungsten such as MoNbTaWV [8], TaNbHfZrTi [9] and WMoCrTiAl [10] because of their excellent mechanical properties at high temperature. High entropy alloys (HEAs) are expected to own improved oxidation resistance of matrix metal due to strongly reduced diffusivity and formation of complexes oxides. O. N. Senkov reported that formation of complex oxides such as $CrTaO_4$, $Ta_{12}MoO_{33}$, $CrNbO_4$ and $Nb_2Zr_8O_{22}$ results in better oxidation resistance of $NbCrMo_{0.5}Ta_{0.5}TiZr$ HEAs as compared with Nb–Si–Al–Ti and Nb–Si–Mo alloys [11]. This result indicates that the reaction between oxides could form complex oxides and the oxidation mechanism has been changed. Therefore, for developing Ta-W based alloys with high oxidation resistance, it is necessary to know the reaction and the compatibility between the oxides.

In this study, the solid reaction among oxides of Ta-W-Al-Si (Ta_2O_5-WO_3-SiO_2-Al_2O_3) are discussed and the phase equilibria of these oxides are investigated at 1200 ºC. Since the liquid phase resulted in oxides layer can protect the alloy from severe oxidation, the liquid phase region of Ta_2O_5-WO_3-Al_2O_3 ternary system in isothermal section 1300 ^oC, 1400 ^oC and 1500 ^oC, is also studied in this work.

2. Experimental

Ta_2O_5 (D50 = 40 μm, purity > 99.9%, Ning Xia Orient Tantalum Industry Co., Ltd., China), WO_3 (D50 = 20 μm, purity > 99.9%, General Research Institute for Nonferrous Metals, Beijing, China) and SiO_2 (D50 = 1 μm, purity > 99.0%, Sinopharm Chemical Reagent Co., Ltd, China)

Al_2O_3 (D50 = 3.5 μm, purity > 99.0%, Sinopharm Chemical Reagent Co., Ltd, China) powders were used as the starting materials. The Ta-W-Al-Si are abbreviated as TWAS series followed with numerical which means the mole proportion. For solid phase reactions, power mixtures with total mass 1.5 grams were mixed by hand with an agate pestle and mortar for 2 hrs using anhydrous ethanol as medium. After being dried, batches of the power mixtures were dry-pressed in a steel mode with inner diameter of 10 mm at 30 MPa for 30 s. And then, each sample was heat treated at high temperature in a sealed Al_2O_3 crucible to avoid mass loss of the volatile substance. For investigating the reaction in binary system, hold time of heat treatment was 6hr; for studying the equilibrium of ternary and quandary systems, holding time was 6hr, 30hr and 72hr, respectively, until phase compositions had no more changes. The sealed specimens were cooled in furnace with in cooling rate of 30^{o}C/min until 500^{o}C then quenched in air.

According to thermodynamic estimation and experimental observations, liquid phase appears in the Ta_2O_5-WO_3-Al_2O_3 powder mixture above 1200 ºC. Liquidus regions in the phase diagrams were determined by observation on melting of the respective samples after heating for 2 h at 1300 - 1500 ºC. The sealed crucibles containing the specimen were quenched into water.

The as-sintered samples were pulverized by hand with an agate pestle and mortar. To avoid the contamination of crucible, the surface of sample was polished carefully by diamond sand paper primarily. Phases presented were identified by X-ray diffractometer (XRD-6000, Shimadzu, Japan) with Cu Kα radiation in a scanning range of 10-80 °. Typical microstructures of the samples and compositions of the phases present were measured using an electron probe X-ray micro-analyzer (EPMA) with wave length dispersive detectors (JXA-8200, JEOL, Japan).

3. Results and discussion

3.1 The reaction and solid solubility of binary system

This system includes Ta_2O_5-WO_3, Ta_2O_5-Al_2O_3, WO_3-Al_2O_3, Ta_2O_5-SiO_2, WO_3-SiO_2 and Al_2O_3-SiO_2 six binary systems. The compositions of binary systems are summarized in Table 1. The reactions of Al_2O_3-SiO_2 binary have been report many times [12,13]. In this binary system, mullite is an important high-temperature structural refractory, due to its good mechanical strength, excellent thermal shock, high creep resistance, low thermal conductivity and high-temperature stability. Solid-state reaction process to synthesize mullite requires extremely high temperature (> 1300 ºC) [14,15]. In this study, no solid reaction was observed at 1200 ºC. The experiments in Ta_2O_5-SiO_2 and WO_3-SiO_2 binary systems showed that no reaction happened in these systems, while, phase transform of hexagonal quartz to tetragonal cristobalite was observed (Fig. 1)[14]. In WO_3-Al_2O_3 binary system, J. L. Waring found that compound $2Al_2O_3 \cdot 5WO_3$ ($Al_4W_5O_{21}$) can be formed [16], while no X-ray diffraction data of this compound can be found in PDF database, and single crystal data indicate that the composition of the compound is Al_2O_3•$3WO_3$ rather than $2Al_2O_3$•$5WO_3$. In this study, compound $Al_2W_3O_{12}$ (Al_2O_3•$3WO_3$) was identified (Fig. 2). As M. G. Zuev reported, after heat treated the oxides of Ta and V, and $Al(OH)_3$ in air(in the sequence of 675 °C, 1000°C, 1200°C, and 1350°C each for 40 h), the compound of $AlTaO_4$ ($Ta_2O_5 \cdot Al_2O_3$) can be formed [17]. In this case, after heat treatment for 6hrs in air, Al_2O_3 and Ta_2O_5 reacted to form $AlTaO_4$, which is confirmed with by M. G. Zuev(as seen in Fig.2).

Three compounds were found in Ta_2O_5-WO_3 binary system, $Ta_{22}W_4O_{67}$, Ta_2WO_8 and $Ta_{16}W_{18}O_{94}$ [18,19]. The reaction between Ta_2O_5 and WO_3 had also been discussed previously [20]. The reactions of binary systems are summarised in Table 2. The crystal lattic parameters formed binary compounds are listed in Table 3.

The solid solubility: Schmid [21] reported a continuous solid solution with a formula of (1-x) Ta_2O_5•xWO_3 at 0-26.7 mol% WO_3. A solid solution was presented in the composition range of SiO_2:Ta_2O_5 from 0 to 1:4 [22]. The addition of Al_2O_3 forms phases structurally similar to low Ta_2O_5 which are stable up to the solidus temperatures, the solubility is less than 6.0mol% [18,23]

3.2 Equlibria in ternary system

The compositions of sample choosen for ternary system is listed in Table 4.

3.2.1 Ta_2O_5-WO_3-Al_2O_3 ternary system

Typical samples were reacted 6 to 72 hr for studying the phase equilibrium in this system and the results are showed in Table 4. Five compounds were formed in this system and five coexisting triangles WO_3-$Al_2W_3O_{12}$-$Ta_{16}W_{18}O_{94}$, $Al_2W_3O_{12}$-$Ta_{16}W_{18}O_{94}$-Al_2O_3, $Ta_{16}W_{18}O_{94}$-Al_2O_3-$AlTaO_4$, $Ta_{16}W_{18}O_{94}$-$AlTaO_4$-Ta_2WO_8 and $AlTaO_4$-Ta_2WO_8-$Ta_{22}W_4O_{67}$ constructed the compatibility relationship of ternary system. Viewed from the back-scattered electron image of typical Ta_2O_5-WO_3-Al_2O_3 ternary system sample, three phases, dark, grey and white were coexisting as shown in Fig. 2. EMPA results showed that the elemental contents of these phases were coincidence with $AlTaO_4$, $Ta_{16}W_{18}O_{94}$, Ta_2WO_8 respectively.

It is interesting that in the sample of TWA 811, only two phases $AlTaO_4$ and Ta_2O_5 are identified. Solid solution is predicted based on binary system results. TWA 81H and TWA810 with alumina content 0.3 and 0 were prepared to compare the solubility of alumina. Only one phase Ta_2O_5 can be found in the XRD pattern, as showed in Fig. 3. Simultaneously, the diffraction peaks of the (1-x)$Ta_2O_5\cdot$xWO_3 were shifted to lower angles, indicating incorporation of Al_2O_3 into the lattice to expand the solid solution along the compositional line of 11$Ta_2O_5\cdot$4WO_3-Al_2O_3. For explanation of the lattice expansion, Al_2O_3 substituted WO_3 with avoidance of forming O vacancies, replacement of 1 mole W with cation radius of 137 pm by 2 mole Al with cation radius of 236 pm would expand the lattice. The phase compatibility relationship and solubility of ternary system are summarized as Fig. 4.

3.2.2 Ta_2O_5-WO_3-SiO_2 ternary system

The phase relationship of Ta_2O_5-WO_3-SiO_2 ternary system had been published previously. [18] Since SiO_2 did not take part in the reactions, the system contained three-phase compatibility regions, one continuous solid solution and a solid solution region.

3.2.3 Ta_2O_5-Al_2O_3-SiO_2 ternary system

Similar with binary system, mullite cannot be formed at 1200 °C, only Al_2O_3-$AlTaO_4$–SiO_2 and $AlTaO_4$–SiO_2-Ta_2O_5 coexisted. While at 1500 °C，XRD patterns of typical samples (Fig. 5) show that due to formation of $Al_6Si_2O_{13}$ (mullite) and $AlTaO_4$, coexisting of $Al_6Si_2O_{13}$, $AlTaO_4$ and SiO_2 in sample TAS 122, $AlTaO_4$,Ta_2O_5 and SiO_2 coexisting in sample TAS 214. No solid solution region was observed in this system. Thus, the compatibilities at 1200 °C and 1500 °C are summarized as Fig. 6. Mullitization samples were annealed at 1200 °C for 6 hours, no decomposition reaction was observed, confirming the stability of mullite phase at 1200 °C.

3.2.4 WO_3-Al_2O_3-SiO_2 ternary system

In the binary system, mullitization temperature was higher than 1200 °C, when WO_3 was added in the system. As XRD patterns of samples WAS 131 and WAS 126 shown that the mullite diffraction (Fig. 7) can be identified, which indicates that mullite formation temperature is 100 °C lower than that required for binary system [19]. It has been reported that mullite formation in reaction sintering couples quartz and Al_2O_3 is controlled by dissolution–precipitation reactions, where Al_2O_3 species dissolve into the SiO_2-rich liquid until a critical Al_2O_3 concentration is reached [24]. Higher Al_2O_3 concentrations induce random mullite nucleation in the bulk of the SiO_2 -rich phase. It was reported that the presence of V_2O_5 could accelerate the mullite phase formation as V_2O_5 could decrease the viscosity of the SiO_2-rich liquid [25]. Although the melting point of WO_3 is higher than 1400 ^oC, the eutectic temperature of Al_2O_3 and WO_3 is lower than 1200 ^oC [17]. In this case, liquid phase can be formed at 1200 ^oC by Al_2O_3-WO_3, the dissolution of Al_2O_3 benefits the formation of mullite.

In the ternary system, compound $Al_2W_3O_{12}$ is also determined (as seen in Fig. 7) and it is compatible with Al_2O_3, mullite, WO_3 and SiO_2 respectively. The compatibility of WO_3-Al_2O_3-SiO_2 is showed in Fig. 8.

3.3 The compatibility of Ta_2O_5-WO_3-Al_2O_3-SiO_2 quaternary system

Based on the compatibility of ternary system, typical samples selected for research the compatibility of quaternary system are listed in Table 5. The XRD analysis results of the samples heated at 1200 ^oC for 6 hr are also listed. No new quaternary compound was found. From the XRD patterns of sample TWAS1111 located in the central of pyramid, the coexisting of $Ta_{16}W_{18}O_{94}$, Ta_2WO_8, $AlTaO_4$, SiO_2 phases could be identified. The tie-line of SiO_2-$AlTaO_4$ established the tetrahedron of $Ta_{16}W_{18}O_{94}$-Ta_2WO_8-$AlTaO_4$-SiO_2. The $Ta_{16}W_{18}O_{94}$, $Al_6Si_2O_{13}$, $Al_2W_3O_{12}$ and Al_2O_3 were coexisted in the sample TWAS14K8, it indicates the tie-line of $Ta_{16}W_{18}O_{94}$-$Al_6Si_2O_{13}$ established the tetrahedron of $Ta_{16}W_{18}O_{94}$-$Al_6Si_2O_{13}$-$Al_2W_3O_{12}$-Al_2O_3 and $Al_2W_3O_{12}$-$Ta_{16}W_{18}O_{94}$-$Al_6Si_2O_{13}$-SiO_2 . The compatibility of Ta_2O_5-WO_3-Al_2O_3-SiO_2 quaternary system is showed in Fig.9.

The solid solution has also been found in ternary system. In the sample TWAS3113, three phases, Ta_2O_5, $AlTaO_4$and SiO_2 were identified, neither the binary nor ternary tungsten oxides were observed. It indicates that the solid solution of tungsten oxides is present. In binary system, the solubility of WO_3, SiO_2 and Al_2O_3 in Ta_2O_5 is 0-26.7 mol%, 0-25.0 mol% and 0-6.0 mol% respectively. In quaternary system, the oxides formed solid solution with Ta_2O_5 primarily until the solid solution limit is reached. That explained the XRD patterns of the sample (TWASX52G) is close to Ta_2O_5, , in which only one phase Ta_2O_5 had been identified (see Fig. 10).

3.4 Liquidus region of Ta_2O_5-WO_3-Al_2O_3 ternary system at 1300 ºC and above

Melting incongruently to $Ta_{22}W_4O_{67}$ plus liquid at about 1580 ^oC was reported in the region near Ta_2O_5 of Ta_2O_5-WO_3 binary system[16], The WO_3-Al_2O_3 binary system has a eutectic temperature at 1190 ºC [14]. No eutectic point was reported in Ta_2O_5-Al_2O_3 binary system.

The compositions of the samples selected to study the liquidus region at 1300-1500 ºC are listed in Table 6. In the experiments, appearance of liquid was judged from the melting behavior of the samples. Although some samples did not melt completely, the characteristic deformation of the samples indicated coexistence of liquid (L) with solid phase (S).

The compositions of the TWA0EB and TWA051 samples are located in the WO_3-Al_2O_3 binary system. Both samples melted completely at 1300 ºC. The ternary sample TWA181 having a composition near this region was also melted. While, liquid present in samples TWA283,TWA285 and TWA151 indicated the liquidus region on the WO_3-Al_2O_3 line at 1300 ºC was set in the compositional range of WO_3 56.0-83.0 mol%.

As the temperature increases, the liquidus region in the phase diagram is expanded, especially in the samples containing a high concentration of WO_3. For example, the liquidus region in the Ta_2O_5-WO_3 system is expanded up to 75.0 mol% WO_3 at 1400 ºC.

The liquid regions of the ternary system at 1300-1500 ºC are shown in Fig. 11. Comparing with liquidus region of Ta_2O_5-WO_3-SiO_2 system, liquid phase region was expanded around WO_3, no liquid phase could be identified in high Al_2O_3 or Ta_2O_5 regions.

4. Conclusion:

(1) The reactions among oxides of Ta-W-Al-Si (Ta_2O_5-WO_3-SiO_2-Al_2O_3) at 1200 ºC are investigated. $Ta_{22}W_4O_{67}$, Ta_2WO_8, $Ta_{16}W_{18}O_{94}$, $Al_2W_3O_{12}$, $AlTaO_4$ can be formed by solid reactions. When reaction temperature was increased to 1500 ºC, mullitization reaction could be found in binary system. Compatibility of $AlTaO_4$ and $Al_2W_3O_{12}$ with each of oxides is demonstrated. Liquid phase formed by Al_2O_3-WO_3 in WO_3-SiO_2-Al_2O_3 benefits the mullitization reaction and mullite can be formed at 1200 ºC in ternary system.

(2) A solid solution with a formula of (1-x) $Ta_2O_5 \cdot xWO_3$ was identified. $Al_2O_3$and SiO_2 could dissolve in the solid solution with a maximum solubility of 25.0% SiO_2 and 6.0% Al_2O_3 respectively.

(3) Liquid phase first appeared in the WO_3-rich corner of the Ta_2O_3-WO_3-Al_2O_3 ternary system at 1300 ºC. As the temperature increased, the liquidus area expands towards the Al_2O_3- and the Ta_2O_5-rich corners. A phase diagram with illustration of the liquidus region was constructed.

Acknowledgment

The authors gratefully acknowledge the financial support provided by NDFC, China (51464001) and project of powder material and advance ceramics state key lab (1401). The author would like to thank Dr. Huang Zhenkun for helpful guide, and Dr. Chen for EMPA analysis.

References

[1] T. Hirai, G. Pintsuk, J. Link, et al. Cracking failure study of ITER-reference tungsten grade under single pulse thermal shock loads at elevated temperatures, J.Nucl.Mater. 757 (2009)

390-391

[2] R. E. Nygren, R. Raffray, D. Whyte, et al. Making tungsten work-ICFRM-14 session T26 paper 501 Nygren et al. making tungsten work, J.Nucl.Mater. 417(2011) 451-456.

[3] H. Yukawa, T. Nambu, Y. Matsumoto. Ta-W alloy for hydrogen permeable membranes, Mater. Trans. 52(4) (2011) 610-613.

[4] P. Kofstad, J. Krudtaa. High temperature metallographic microscope studies of the initial oxidation of tantalum, Journal of the Less Common Metals. 5(1963) 477-492.

[5] V. B. Voitovich, V. A. Lavrenko, V. M. Adejev, et al. High-temperature oxidation of tantalum of different purity, Oxid. Met. 43(1995) 509-526.

[6] V. A. Avincola, M. Janek, U. Stegmaier, et al. Tantalum oxidation in steam atmosphere, Oxid. Met. 85(2016) 459-487.

[7] A.Bhowmik, H.J.Stone. A study on the influence of Mo, Al and Si additions on the microstructure of annealed dual phase Cr–Ta alloys, J. Mater. Sci. 48(2013) 3283-3293.

[8] O. N. Senkov, G. B. Wilks, J. M. Scott, et al. Mechanical properties of $Nb_{25}Mo_{25}Ta_{25}W_{25}$, and V_{20} $Nb_{20}Mo_{20}Ta_{20}W_{20}$ refractory high entropy alloys, Intermetallics, 19(2011) 698-706.

[9] O. N. Senkov, J. M. Scott, S. V. Senkova, et al. Microstructure and room temperature properties of a high-entropy TaNbHfZrTi alloy, J. Alloys Compd. 509(2011) 6043-6048.

[11] O. N. Senkov, S. V. Senkova, D. M. Dimiduk, et al. Oxidation behavior of a refractory $NbCrMo_{0.5}$ $Ta_{0.5}TiZr$ alloy, J. Mater. Sci. 47(2012) 6522-6534.

[12] J. A. Pask. Stable and metastable equilibria in the system SiO_2-Al_2O_3, J. Amer. Chem. Soc. 58 (1975):507-512.

[13] J. A. Pask, A. P. Tomsia. Formation of mullite from sol-gel mixtures and kaolinite, J. Amer.

Chem. Soc. 74 (2010):2367-2373.

[14] M. Imose, A. Ohta, Y. Takano, et al. Low-Temperature Sintering of mullite/yttria-Doped zirconia composites in the mullite-rich region, J. Amer. Chem. Soc. 81(2010) 1050-1052.

[15] H. A. Wriedt. The O-Pu (oxygen-plutonium) system, Bull. Alloy Phase Diagr. 11(1990) 184-202.

[16] J. L. Waring. Phase equilibria in the system aluminum oxide—tungsten oxide, J. Amer. Chem. Soc. 48(1965) 493-493.

[17] M.G.Zuev. Phase ratios in Al_2O_3-V_2O_5-Ta_2O_5 system in subsolidus range, Zh. Neorg. Khim. 39(1994) 512-513

[18] R. S. Roth, J. L. Waring. Phase equilibria as related to crystal structure in the system niobium pentoxide-tungsten trioxide, J.res.natl.bur.stand, , 70A(1966).

[19] R. S. Roth, J. L. Waring, H. S. Parker. Effect of oxide additions on the polymorphism of tantalum pentoxide. IV. The system Ta_2O_5-Ta_2WO_8, J. Solid State Chem. 2(1970) 445-461.

[20 H.Y. Wang, Y. H. Chen, Z. J. Bai, et al. Phase relations in the Ta_2O_5-WO_3-SiO_2 system, Int. J. Refract. Met. Hard Mater. 1 (2017) 47–51

[21] S. Schmid, R. L. Withers, J. G. Thompson. The incommensurately modulated(1-x)Ta_2O_5·xWO_3, 0≤x,≤0.267 solid solution, J. Solid State Chem. 99(1992) 226-242.

[22]D. A. Reeve, N. Bright. Phase relations in the system CaO-Ta_2O_5-SiO_2, J. Amer. Chem. Soc. 52(1969) 405-409.

[23] D. T. Murphy, V. Fung, S. Schmid. Structural investigation of the incommensurate modulated Ta_2O_5· Al_2O_3 System, Aperiodic Crystals, Springer, Dordrecht, 2013.

[24] S. H. Hong, W. Cermignani, G. L. Messing. Anisotropic grain growth in seeded and

B_2O_3-doped diphasic mullite gels, J. Eur. Ceram. Soc. 16(1996):133-141.

[25] L. B. Kong, Y. B. Gan, J. Ma, et al. Mullite phase formation and reaction sequences with the presence of pentoxides, J. Alloys Compd. 351(2003) 264-272.

5. Tables and Table captions

Table 1 The sample compositions for binary system at 1200°C

Sample	Composition (mole)				Phase component
	Ta_2O_5	WO_3	Al_2O_3	SiO_2	
TW X5	33	5	0	0	Ta_2O_5(ss)
TW 85	8	5	0	0	$Ta_{22}W_4O_{67}$,Ta_2WO_8
TW 7L	7	10	0	0	Ta_2WO_8,$Ta_{16}W_{18}O_{94}$
TW 15	1	5	0	0	$Ta_{16}W_{18}O_{94}$,WO_3
WA 11	0	1	1	0	$Al_2W_3O_{12}$,WO_3,Al_2O_3
TA 11	1	0	1	0	$AlTaO_4$,Ta_2O_5,$Ta_{0.703}O_{1.65}$
WS 11	0	1	0	1	WO_3, SiO_2
AS 11	0	0	1	1	Al_2O_3, SiO_2

Note: X-33 mole proportion, L-10 mole proportion.

Table 2 the reactions of binary systems

Binary system	Reactions at 1200 °C	Reference
Al_2O_3-SiO_2	No reaction	[12,13]
Ta_2O_5-Al_2O_3, ,	$Ta_2O_5+Al_2O_3 \rightarrow 2AlTaO_4$	[15]
Ta_2O_5-WO_3	$11Ta_2O_5 + 4WO_3 \rightarrow Ta_{22}W_4O_{67}$	
	$Ta_2O_5 + WO_3 \rightarrow Ta_2WO_8$	[16,17]
	$8Ta_2O_5 + 18WO_3 \rightarrow Ta_{16}W_{18}O_{94}$	
Ta_2O_5-SiO_2	$Ta_2O_5 + SiO_2 \rightarrow Ta_2O_5ss$	[14]
WO_3-Al_2O_3,	$3WO_3+Al_2O_3 \rightarrow Al_2W_3O_{12}$	[14]
WO_3-SiO_2	No reaction	[14]

Table 3 The crystal lattice parameters of binary compounds

compound	PDF number	Cell parameter											
		Picked up from PDF card						Detected value from sample					
		a	b	c	α	β	γ	a	b	c	α	β	γ
$Ta_{16}W_{18}O_{97}$	29-1323	12.28	12.28	3.88	90°	90°	90°	12.23	12.23	3.86	90°	90°	90°
Ta_2WO_8	29-1322	16.70	3.88	8.86	90°	90°	90°	16.73	3.87	8.82	90°	90°	90°
$Ta_{22}W_4O_{67}$	29-1325	3.84	47.40	6.13	90°	90°	90°	3.84	47.34	6.09	90°	90°	90°
$AlTaO_4$	25-1490	6.13	7.38	8.72	90°	90°	90°	6.11	7.35	8.80	90°	90°	90°
$Al_6Si_2O_{13}$	15-0776	7.55	7.69	2.88	90°	90°	90°	7.61	7.73	2.87	90°	90°	90°
$Al_2W_3O_{12}$	76-1658	12.59	9.05	9.12	90°	90°	90°	12.50	8.97	9.07	90°	90°	90°

Table 4 The sample compositions for ternary system

Sample	Composition (mole)				Phase component	
	Ta_2O_5	WO_3	Al_2O_3	SiO_2	1200 °C	1500 °C
TWA810	8	1	0	0	Ta_2O_5（ss）	
TWA81H	8	1	0.3	0	Ta_2O_5（ss）	
TWA421	4	2	1	0	$Ta_{22}W_4O_{67}$, $AlTaO_4$, Ta_2WO_8	
TWA331	3	3	1	0	$Ta_{16}W_{18}O_{94}$, $AlTaO_4$,Ta_2WO_8	
TWA 113	1	1	3	0	$Ta_{16}W_{18}O_{94}$,$AlTaO_4$,Al_2O_3	
TWA189	1	8	9	0	$Ta_{16}W_{18}O_{94}$, Al_2O_3, $Al_2W_3O_{12}$	
TWAG81	0.5	8	1	0	$Ta_{16}W_{18}O_{94}$,WO_3,$Al_2W_3O_{12}$	
TWA811	8	1	1	0	$AlTaO_4$,Ta_2O_5（ss）	
TWSX52	33	5	0	2	Ta_2O_5(SS)	
TWS852	8	5	0	2	$Ta_{22}W_4O_{67}$, Ta_2WO_8, SiO_2	
TWS7L4	7	10	0	4	Ta_2WO_8, $Ta_{16}W_{18}O_{94}$, SiO_2	
TWS152	1	5	0	2	$Ta_{16}W_{18}O_{94}$, WO_3, SiO_2	
TWS X5X	33	5	0	33	Ta_2O_5 (SS), SiO_2	
TAS122	1	0	2	2	Al_2O_3 ,$AlTaO_4$,SiO_2	$Al_6Si_2O_{13}$,$AlTaO_4$,SiO_2
TAS 16C	1	0	6	12	Al_2O_3 ,$AlTaO_4$,SiO_2	$Al_6Si_2O_{13}$,$AlTaO_4$,SiO_2
TAS214	2	0	1	4	$AlTaO_4$,Ta_2O_5,SiO_2	$AlTaO_4$,Ta_2O_5,SiO_2
TAS141	1	0	4	1	SiO_2 ,$AlTaO_4$,Al_2O_3	$Al_6Si_2O_{13}$,$AlTaO_4$,Al_2O_3
WAS131	0	1	3	1	Al_2O_3,$Al_2W_3O_{12}$,$Al_6Si_2O_{13}$	
WAS126	0	1	2	6	SiO_2,$Al_2W_3O_{12}$,$Al_6Si_2O_{13}$	
WAS513	0	5	1	3	SiO_2,WO_3,$Al_2W_3O_{12}$	

Note: H-0.3 mole proportion, G-0.5 mole proportion, X-33 mole proportion, L-10 mole proportion, C-12 mole proportion.

Table 5 Phase components of quaternary system at 1200 ^{o}C

Sample	Composition (mole)				Phase component
	Ta_2O_5	WO_3	Al_2O_3	SiO_2	
TWAS1919	1	9	1	9	$Al_2W_3O_{12}$, $Ta_{16}W_{18}O_{94}$, WO_3, SiO_2
TWAS1444	1	4	4	4	$Al_2W_3O_{12}$, $Ta_{16}W_{18}O_{94}$, $Al_6Si_2O_{13}$, SiO_2
TWAS14K8	1	4	20	8	$Ta_{16}W_{18}O_{94}$, $Al_6Si_2O_{13}$, $Al_2W_3O_{12}$, Al_2O_3
TWAS3113	3	1	1	3	Ta_2O_5 (ss), $AlTaO_4$,SiO_2
TWAS1111	1	1	1	1	$Ta_{16}W_{18}O_{94}$, Ta_2WO_8, $AlTaO_4$,SiO_2
TWASX52G	33	5	2	0.5	Ta_2O_5 (ss)

Note: K-20 mole proportion, G-0.5 mole proportion.

Table 6 Sample compositions and XRD analysis result after sintering at 1300-1500 ºC

Sample	Composition (mole)			Phase component at different temperatures. L = liquid and S = solid		
	Ta_2O_5	WO_3	Al_2O_3	1300	1400	1500
TWA181	1	8	1	L		
TWA283	2	8	3	L+S		
TWA144	1	4	4	S		
TWA0EB	0	14	11	L		
TWA051	0	5	1	L		
TWA285	2	8	5	L+S		
TWA151	1	5	1	L+S		
TWA483	4	8	3		L+S	
TWA486	4	8	6		L+S	
TWA491	4	9	1		L+S	
TWA145	1	4	5		L+S	
TWA1Y1	1	18	1		L	
TWA553	5	5	3			L+S
TWA441	4	4	1			L+S
TWA445	4	4	5			L+S
TWA236	2	3	6			S
TWA583	5	8	3			L
TWA587	5	8	7			L
TWA471	4	7	1			L

Note: E-14 mole proportion, B-11 mole proportion, Y-18 mole proportion.

6. Figure captions

Fig. 1 XRD pattern of samples TA 11and WA 11

Fig. 2 BSE and EMPA analysis of typical Ta_2O_5-WO_3-Al_2O_3 sample after reacted 6h at 1200°C

Fig. 3 XRD pattern of sample TWA 811， TWA81H and TWA810

Fig. 4 The phase compatibility and solubility in Ta_2O_5-WO_3-Al_2O_3 system

Fig. 5 XRD pattern of samples TAS 141， TAS214 and TAS122

Fig. 6 The phase compatibility of Ta_2O_5-Al_2O_3-SiO_2 system (left1200°C, right 1500°C)

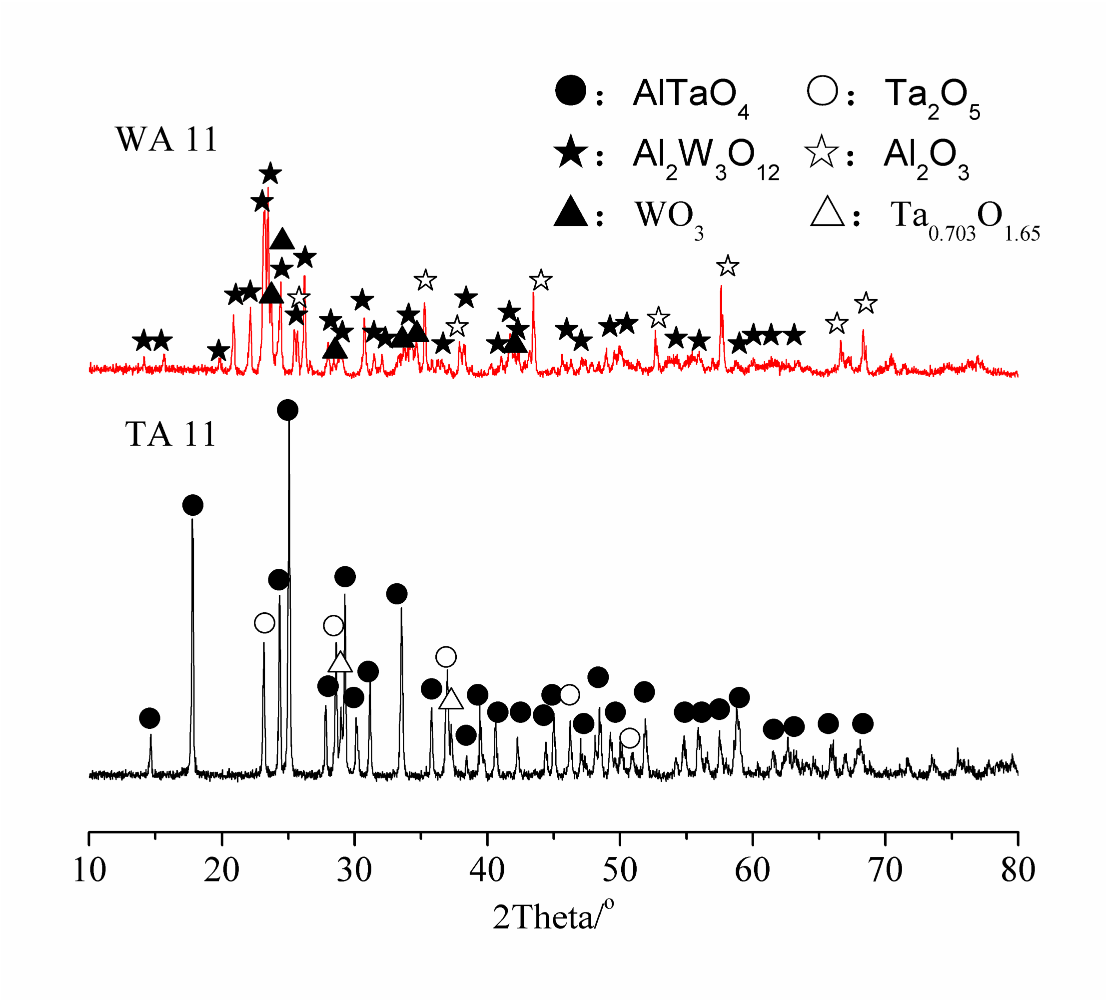
Fig. 7 XRD pattern of formation of mullite in WO_3-Al_2O_3-SiO_2 system at 1200 °C

Fig. 8 The compatibility of WO_3-Al_2O_3-SiO_2 ternary system

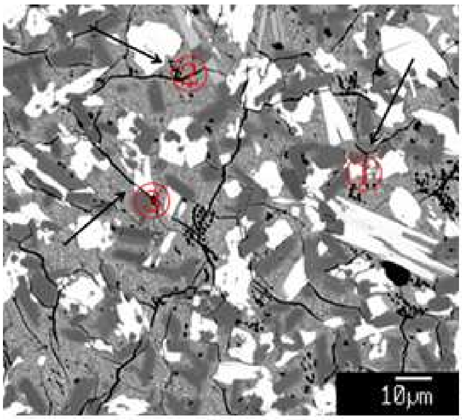
Fig. 9 The phase compatibility and solubility in Ta_2O_5-WO_3-Al_2O_3-SiO_2 system

Fig. 10 XRD pattern of samples TWASX52G

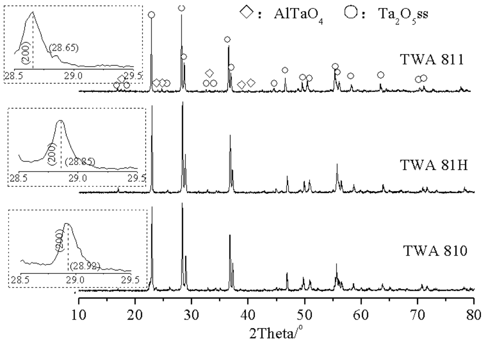
Fig. 11 Liquidus region of Ta_2O_5-WO_3-Al_2O_3 ternary system at 1300 ºC-1500 ºC

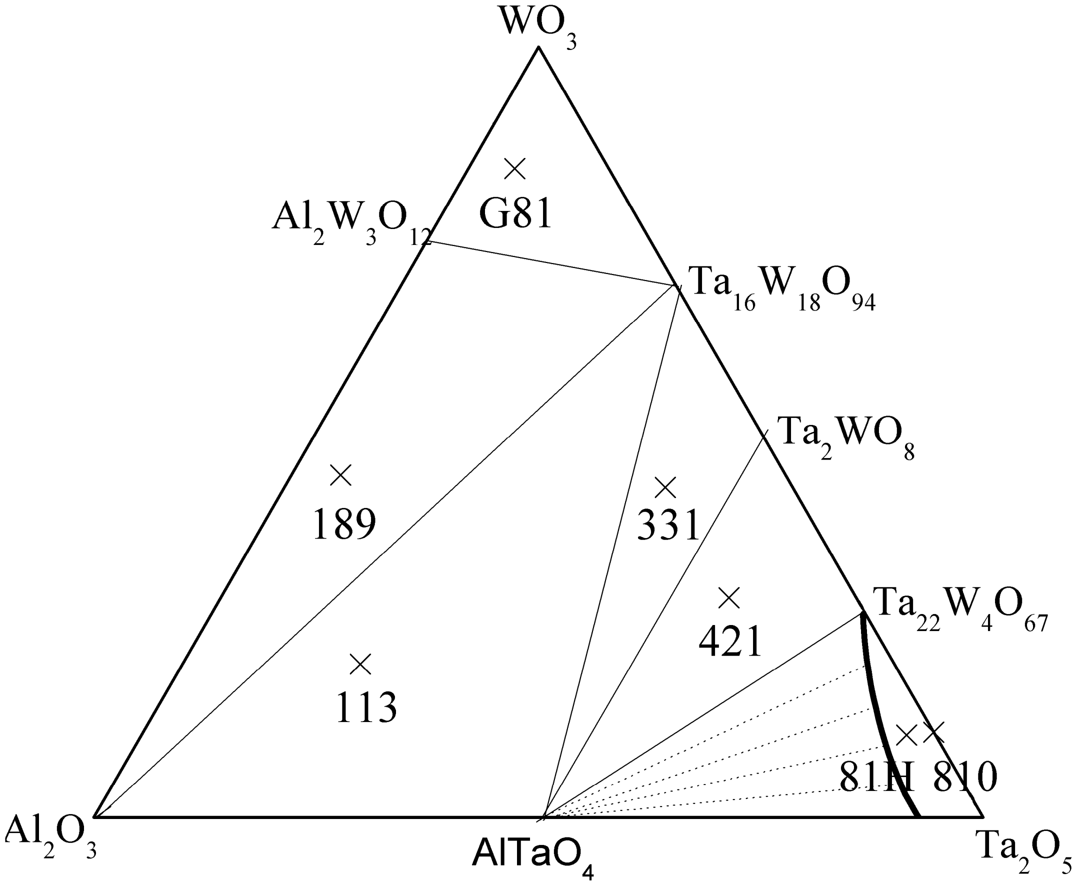


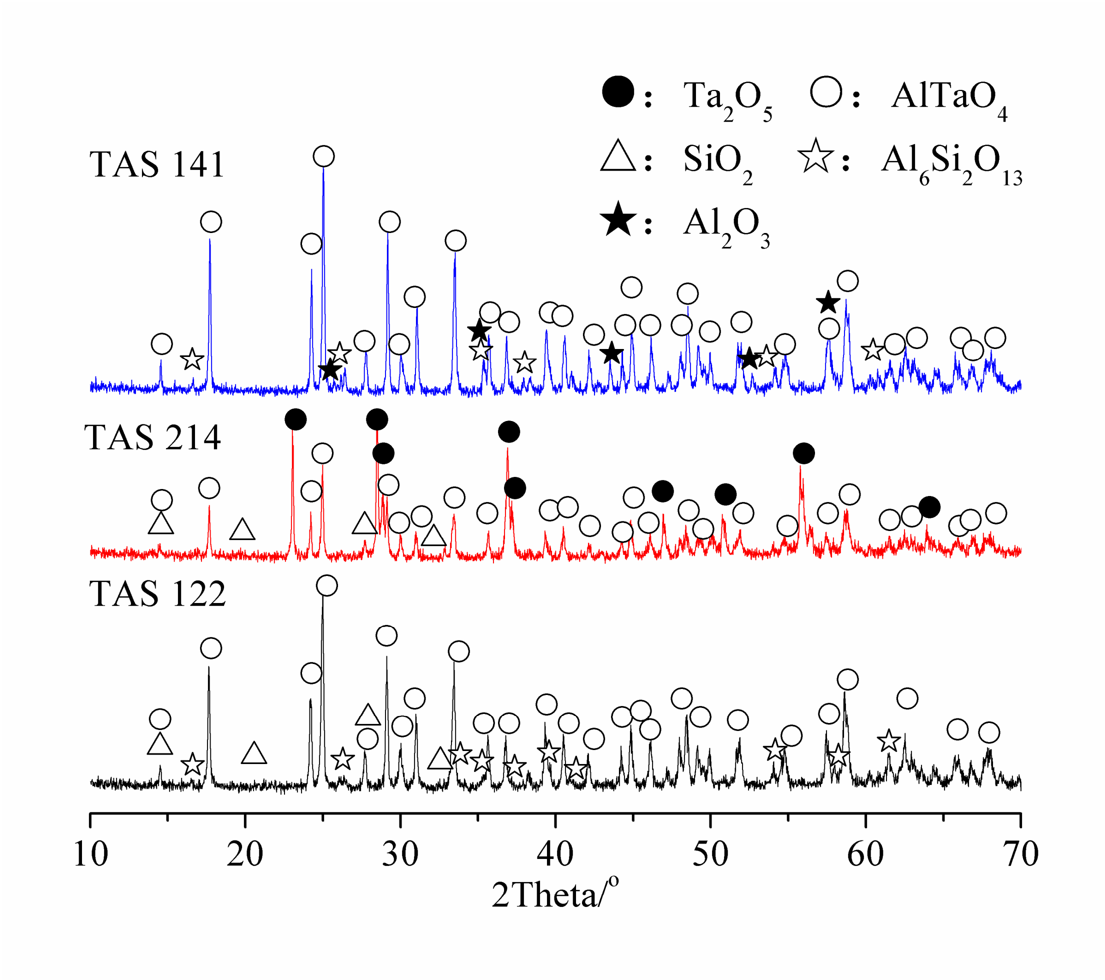
●: AlTaO4
○: Ta2O5
★: Al2W3O12
☆: Al2O3
▲: WO3
△: Ta0.703O1.65
WA 11
TA 11
10
20
30
40
50
60
70
80
2Theta/°



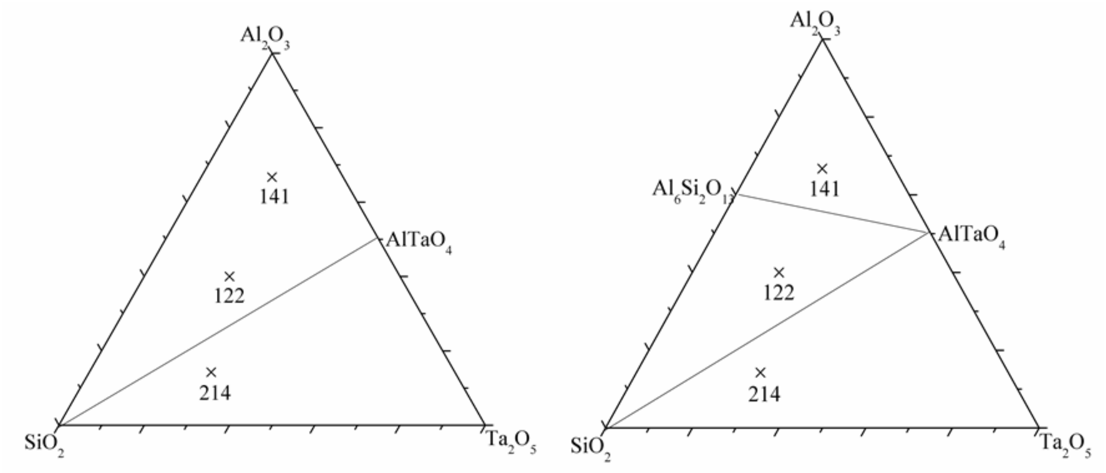
Phase	Composition (mole%)		
	Ta_2O_5	WO_3	Al_2O_3
(1)white	52.4	47.3	0.3
(2)grey	30.6	68.3	1.1
(3) dark	47.7	1.2	51.1


◇: AlTaO4 ○: Ta2O5ss
TWA 811
TWA 81H
TWA 810
(200)
(28.65)
(28.85)
(300)
(28.98)
28.5
29.0
29.5
10
20
30
40
50
60
70
80
2Theta/°

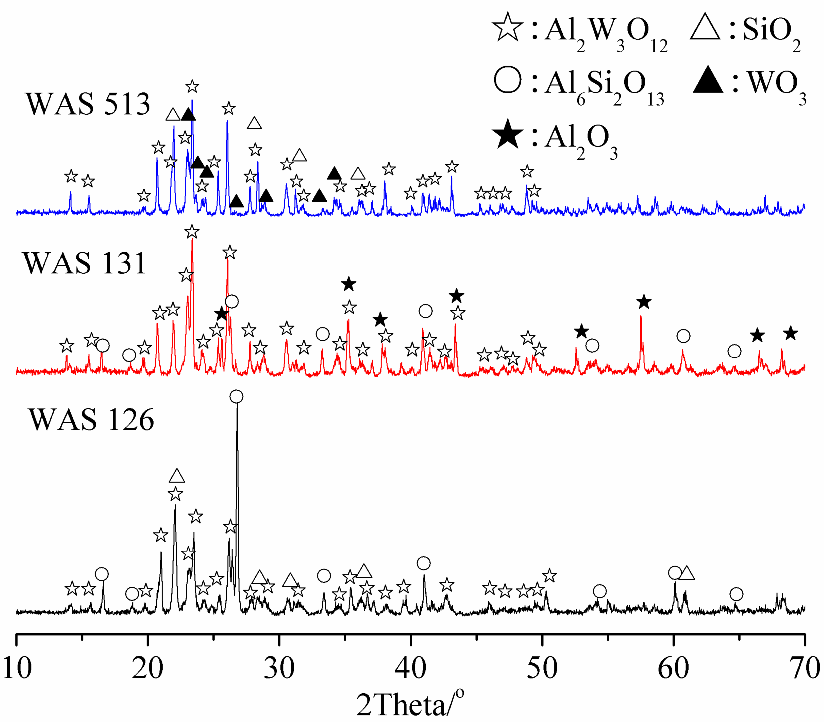

WO_3
G81
$Al_2W_3O_{12}$
$Ta_{16}W_{18}O_{94}$
Ta_2WO_8
189
331
421
$Ta_{22}W_4O_{67}$
113
81H
810
Al_2O_3
$AlTaO_4$
Ta_2O_5

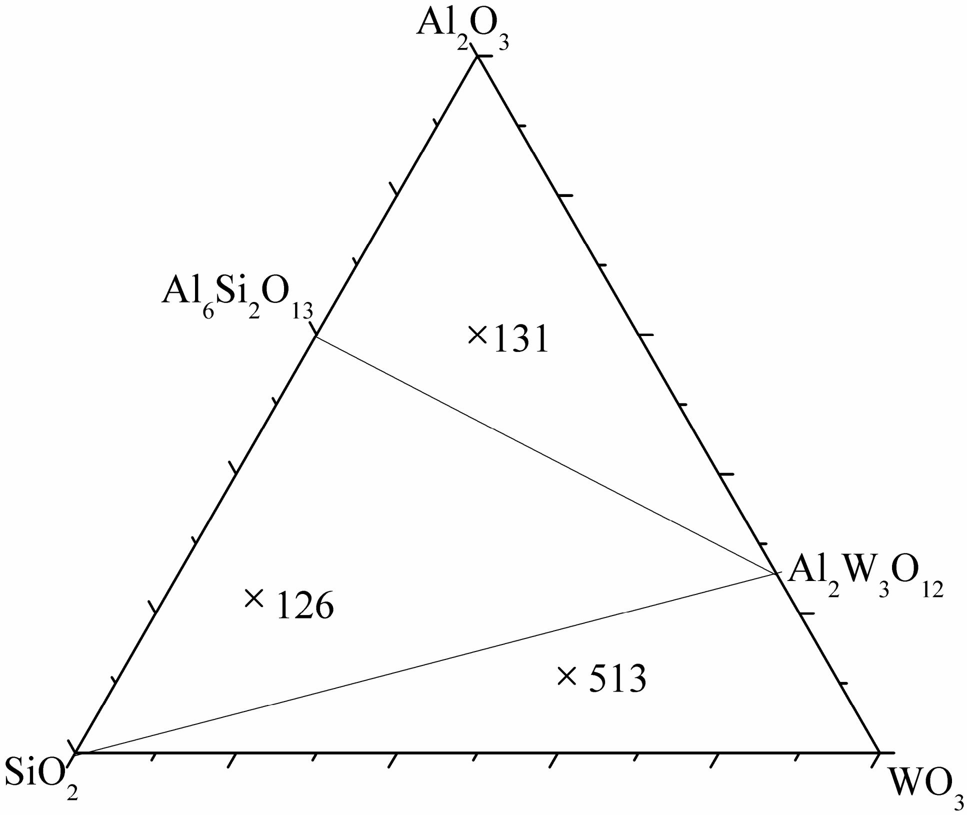


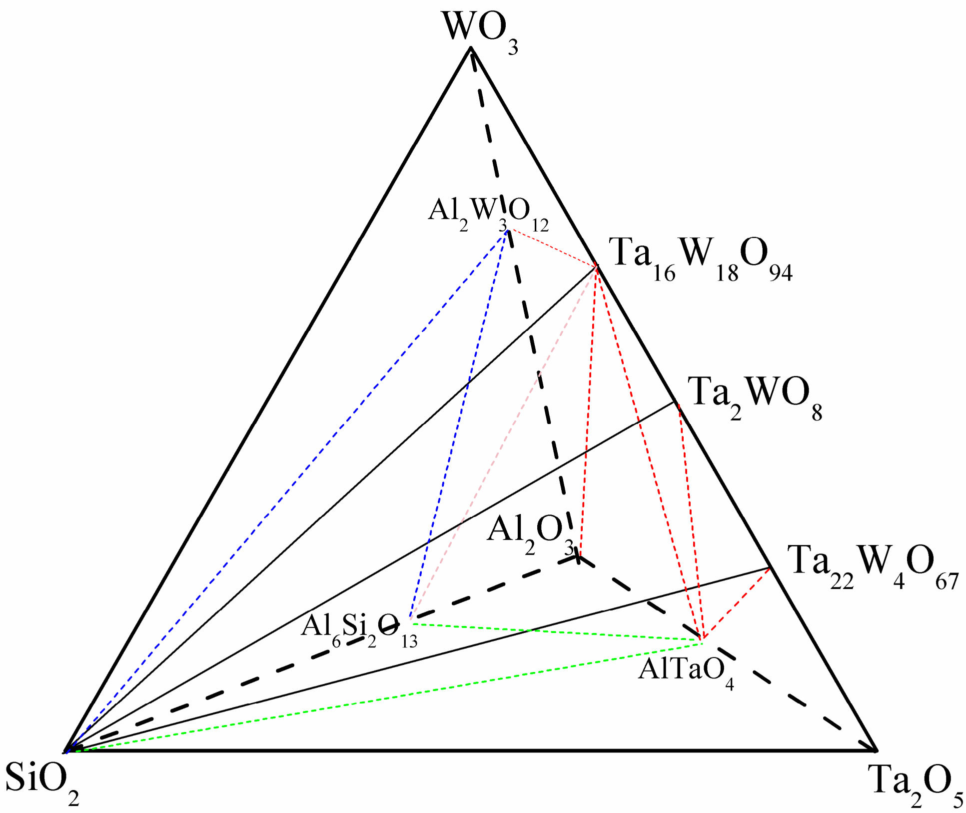
●: Ta2O5
○: AlTaO4
△: SiO2
☆: Al6Si2O13
★: Al2O3
TAS 141
TAS 214
TAS 122
10
20
30
40
50
60
70
2Theta/°



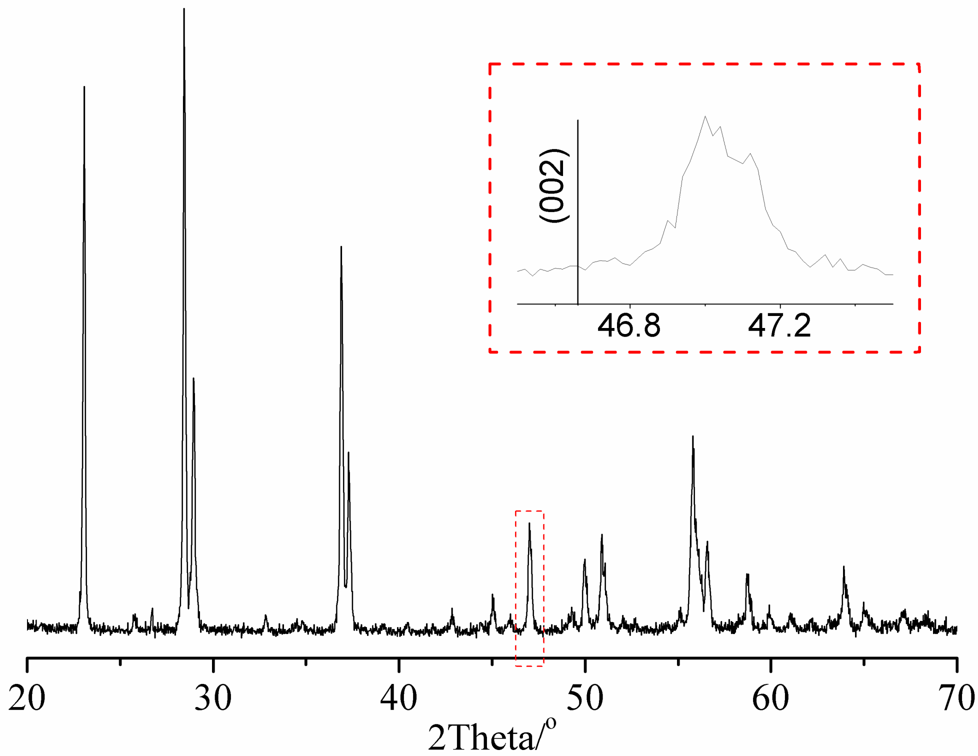
Al2O3
141
AlTaO4
122
214
SiO2
Ta2O5
Al2O3
Al6Si2O13
141
AlTaO4
122
214
SiO2
Ta2O5

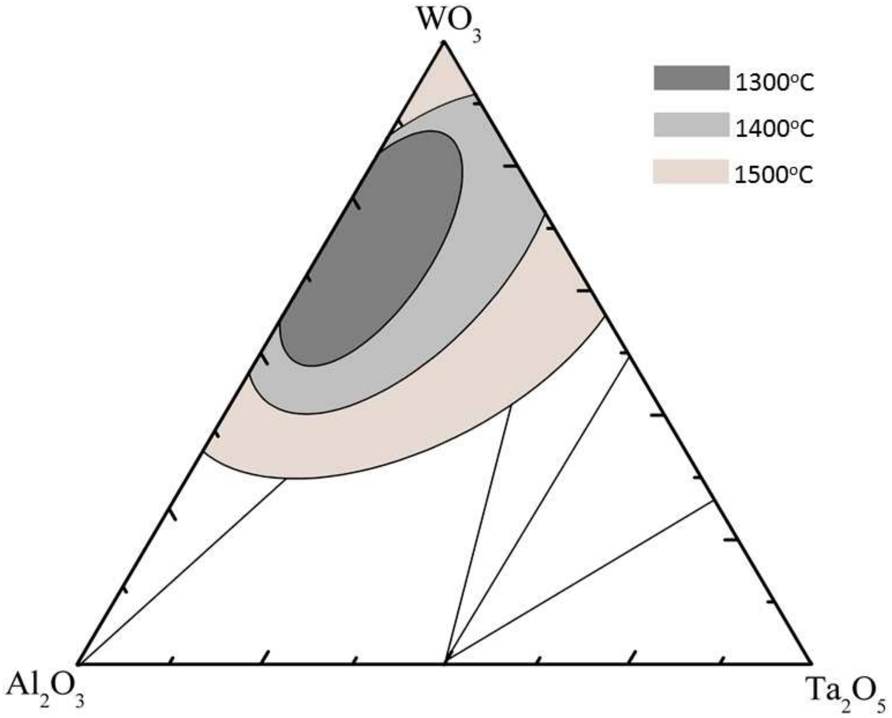

☆ : Al2W3O12
△ : SiO2
○ : Al6Si2O13
▲ : WO3
★ : Al2O3
WAS 513
WAS 131
WAS 126
10
20
30
40
50
60
70
2Theta/°


Al2O3
Al6Si2O13
×131
Al2W3O12
×126
×513
SiO2
WO3



WO3
Al2W3O12
Ta16W18O94
Ta2WO8
Al2O3
Ta22W4O67
Al6Si2O13
AlTaO4
SiO2
Ta2O5


(002)
46.8
47.2
20
30
40
50
60
70
2Theta/°



WO3
1300oC
1400oC
1500oC
Al2O3
Ta2O5

We think that three aspects of the manuscript make it interesting to the research community.

(1) Formation of solid solution among Ta_2O_3, WO_3, Al_2O_3 and SiO_2 is proposed.

(2) The equilibria of ternary systems are constructed, based on these results the subsolidius equilibrium diagram is established.

(3) The liquid region was experimentally determined in the Ta_2O_3-WO_3-Al_2O_3 ternary system in the temperature range of 1300-1500 ºC.

(4) Mullitization can be reacted at 1200 ºC in WO_3-SiO_2-Al_2O_3 ternary system.