

COMPOSITION AND MICROSTRUCTURE OF $MgAl_2O_4$ -W COMPOSITE OBTAINED BY ALUMINOTHERMIC REACTION UNDER COKE PROTECTION

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MgAl₂O₄-W composite was synthesized by aluminothermic reducing method using Al, WO₃, MgO and corundum as raw materials under coke protection. The effects of temperature, content of corundum on the synthesis of MgAl₂O₄-W composite and lattice parameter of spinel has been discussed. The differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis indicated that spinel began to form at 1058.2°C without corundum and shifted to 1120.7°C with 0.8 mol of corundum. The XRD analysis confirmed that spinel and tungsten are the main phases under coke protection. Alumina rich spinel with a high solubility of alumina was easily formed because of the high exothermic heats. The solubility limit of Al₂O₃ in spinel is reached when corundum content is 2.1 mol. Furthermore, the calculated lattice parameter of spinel increases with the increment of added corundum content and rising of temperature. Microstructural observation indicates that cubic tungsten located at grain boundaries of well crystallized spinel. Residual WO₃ has needle like morphology.

INTRODUCTION

Spinel $MgAl_2O_4$ has high hardness, high melting point, good chemical stability and low thermal expansion coefficient. Because of the good physical, chemical, and thermal properties, $MgAl_2O_4$ spinel has a wide range of application in the lining of the steel ladle, transition and burning zones of cement rotary kilns, checker work of the glass furnaces and others [1-7]. Spinel, especially alumina rich spinel, can trap FeO in the molten slag to form (Mg, Fe) Al_2O_4 solid solution, suppressing the slag penetration. Hence the slag resistance of the refractories is improved with introduction of spinel.

Tungsten has high melting point (3395°C), high Young's modulus ($E = 390$ -410 GPa at 20°C) and thermal conductivity (97.1 W/cmK at 10°C). So it is widely used in illumination, electronics, and heat-resistant structure material. Recently, tungsten has been introduced into ceramic as a toughening phase [8-11]. Moreover, tungsten doesn't react with molten slag. These properties make the combination of tungsten and spinel has potential prospect in the refractories and other area, for example,

slide gate, protection tube of thermocouple for measuring steel liquid temperature and other some key parts of refractories for metallurgical industry. May be tungsten can improve wear resistance and thermal spalling resistance. Recently, products made from Al_2O_3 -Cr and Al_2O_3 -W cermet have been prepared as protection tube of thermocouple for measuring the temperature of the melting steel.

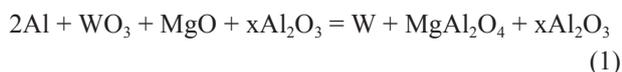
The metallothermic reducing method has been used for a long time to prepare various metals and alloys [12-18]. The reaction released a great amount of heat, which can supply the high temperature needed for the reduction of oxides. In order to control the reaction rate and obtain controllable microstructure, diluent was often added. We have prepared Al_2O_3 -W composite via aluminothermic reaction [19-22]. The application Al_2O_3 -W composite in thermocouple was also studied [23].

In this paper, reaction $2Al + WO_3 + MgO + xAl_2O_3$ in argon and under coke protection is studied. Possibility of formation of alumina rich spinel at lower temperature and the relationship between Al_2O_3 content and the lattice parameters of the spinel were also discussed.

EXPERIMENTAL

The following powders were used in the present study: Metal aluminum (200 mesh, >98.45 wt.%), yellow tungsten oxide (<10 μm , WO_3 : 99.98 wt.%, from Ganzhou Jiangxi Province, P. R. China.), white fused corundum (Al_2O_3 : 98.19 wt.%; Na_2O : 0.55 wt.%).

The overall reaction of this composite formation reaction is:



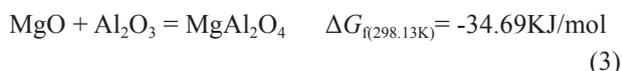
where $x = 0, 0.4, 0.8, 1.4, 2.1$ mol, respectively and MgO content kept unchanged in the process. The starting mixed powders were weighed separately according to the predetermined ratio and then dry mixed in a QMS planetary mill for 60 min. Then the mixed powder was uniaxially pressed into pellets of 20 mm diameter and 12-20 mm height under the pressure of 100Mpa. Samples were dried for 24 h at 110°C and calcined at various firing temperatures for 3h under coke protection. The specimens were separated from coke granules by fused spinel powder to eliminate the influence of carbon and CO. Coke protection is a common and low cost method for carbon containing refractories from oxidization than inert atmosphere.

The phase identification of the composite was determined by X-ray diffraction analysis (XRD) using $\text{CuK}\alpha$ radiation (Philips X'pert diffractometer, Netherlands). The differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis (Netzsch 449C, Germany) were used to determine the formation temperature of spinel. The lattice parameter of spinel was calculated by a crystal cell parameters refinement program for powder X-Rays or neutron diagram, using a least squares refinement method. The microstructures, the morphology and the composition of the crystal were identified by scanning electron microscopy (SEM) (model Philips XL30 TMP) with an energy dispersive scanning attachment for qualitative microanalysis of the coexisting phases (EDAX Phoenix)

RESULTS AND DISCUSSION

Thermal analysis

The overall reaction shown in equation 1 is believed to take place as a combination of following sequential reactions:



The reaction (2) is a typical aluminothermic reaction and easily to happen and finished very quickly. The

reaction (3) is an solid-solid phase reaction and take place at about 1000°C. Part or all of the added corundum will dissolve into spinel. Figure 1 gives the DSC-TG results of the mixture with a 2:1:1:0 mole ratio of Al, MgO, WO_3 and Al_2O_3 heated in Ar at 10°C/min up to 1500°C. The TG curve of figure 1 showed that the mass of the sample decreased from 25°C to 500°C because of the vaporization of WO_3 . The mass started increasing from 500°C to 1500°C, which is attributed to oxidization of Al or W with O_2 in Ar. The DSC curve of the mixture up to 1500°C showed a shallow exotherm from about 980°C to 1200°C which means the formation of MgAl_2O_4 . The peak of MgAl_2O_4 at 1058.2°C is very sharp and narrow, which means MgAl_2O_4 well crystallized. However, the reaction (2) corresponding to the instant reduction of WO_3 was not recorded by the DSC curve. The reaction is too quick for analyzer to record it. Figure 2 give the result of the mixture with 0.8mol white fused corundum heated at the same condition with the Figure 1. Comparing Figure 2 with 1, it is evident that the formation peak of spinel shifted from 1058.2°C to 1120.7°C and the peak is more wider and broader. The endothermic peaks at about 657°C in figure 1 and at 654.2°C in Figure 2 was caused by the melting of aluminum.

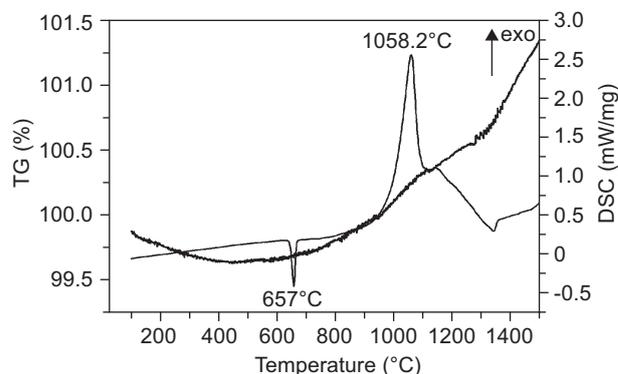


Figure 1. DSC-TG curve of the mixture with $x = 0$ mol.

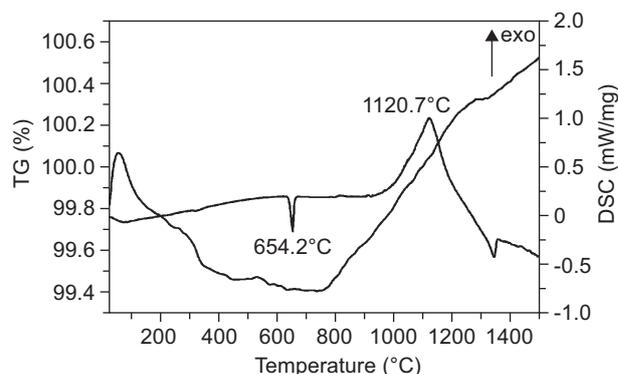


Figure 2. DSC-TG curve of the mixture with $x = 0.8$ mol.

From the DSC-TG curve, we can see that MgO and Al₂O₃ are not only as diluent to control the reaction rate, but also as reactants for the formation of spinel. Furthermore, relative content of MgO to Al₂O₃ will effects the microstructure and crystalline state of spinel.

Phase composition

Because tungsten is easily to react with CO or carbon to form of tungsten carbide, the specimens were separated from coke granules with fused spinel superfine powder. Figure 3 gives the XRD patterns of specimens calcined at 1100 and 1200°C under coke protection, respectively. It seems that there isn't obvious difference between the XRD patterns at 1100°C and those at 1200°C. Spinel and tungsten were the dominant phases. It is noteworthy that no free corundum or fused magnesia was detected in any of the XRD patterns, which means that corundum and fused magnesia have been completely

dissolved into MgAl₂O₄. It is evident from figure3 that spinel is well crystallized from the relatively higher intensity and sharpness of its XRD lines. Furthermore, shifts in the d-spacing of the MgAl₂O₄ lines occurred in all samples, compared with the standard diffraction pattern of stoichiometric spinel (JCPDS 75-1795), which also means that solid solution has taken place during heating.

Variation of lattice parameter

Figure 4 gives the lattice parameter a₀ value of the MgAl₂O₄ and tungsten phases as calculated from XRD patterns in Figure 3, respectively. For convenience, the theoretical value of the stoichiometric spinel and tungsten were plotted. The a₀ value is always smaller than that of stoichiometric spinel (0.8080 nm, from JCPDS 75-1795). At 1100°C, when corundum increases from 0 mol to 1.4 mol, a₀ value of spinel decreased quickly from

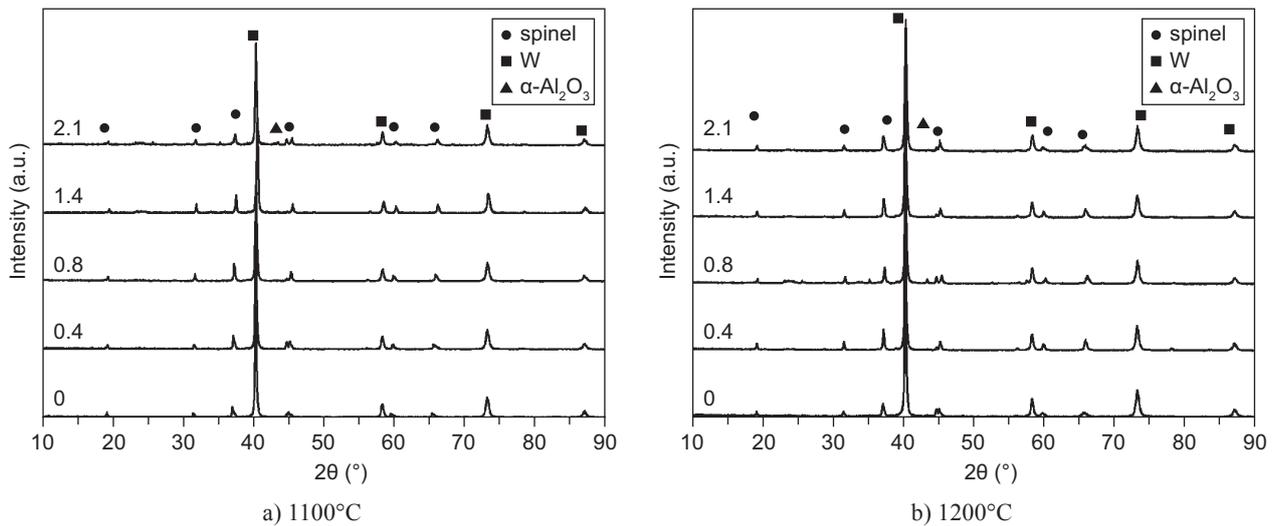


Figure 3. XRD patterns of specimens with different corundum content calcined at various temperatures.

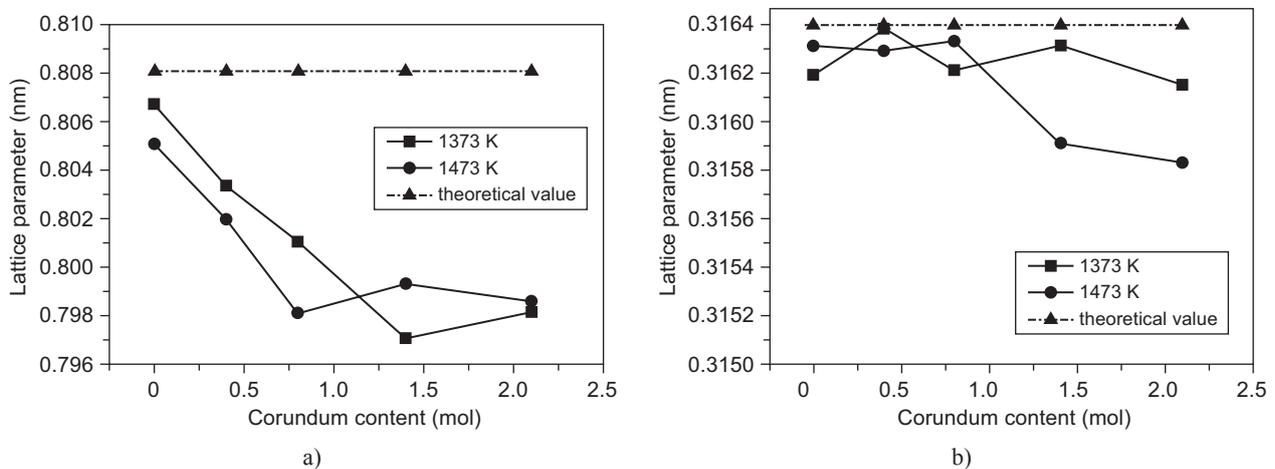


Figure 4. Lattice parameter of spinel (a) and tungsten (b) calculated from XRD patterns in Figure 3.

0.80672 nm to 0.79707 nm, but increased lightly when corundum content increased from 1.4 mol to 2.1 mol. At 1200°C, a_0 value decreased rapidly from 0.80508nm to 0.79811nm with an increase of corundum from 0 mol to 0.8 mol, but the a_0 value varied slightly when corundum content is more than 0.8 mol.

From Figure 4b, it seems that there is not obvious relationship between the lattice parameter of tungsten with corundum content. However, a_0 value is always smaller than the theoretical value of the tungsten(0.3164nm from JCPDS 04-0806).

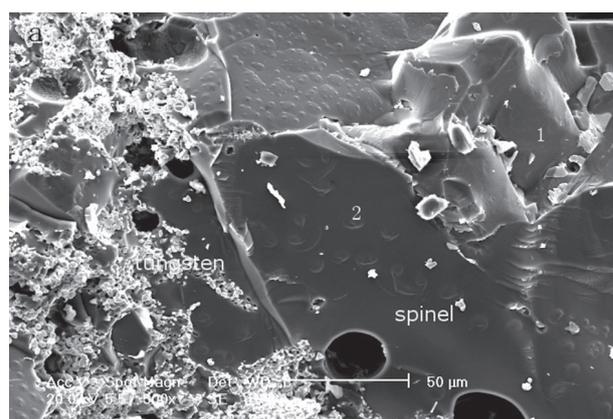
Microstructure and microanalysis

SEM micrographs of the samples containing various corundum are shown in Figure 5. Tungsten (light phase) can be easily distinguished from spinel (dark phase). The particles size of spinel grains varies in a wide range of 20-500µm. The EDS results of the points in 1, 2 and 3 are summarized in Table 1 and the calculated value of the spinel is also listed in the table. It is assumed that all of the Al_2O_3 has been dissolved in spinel.

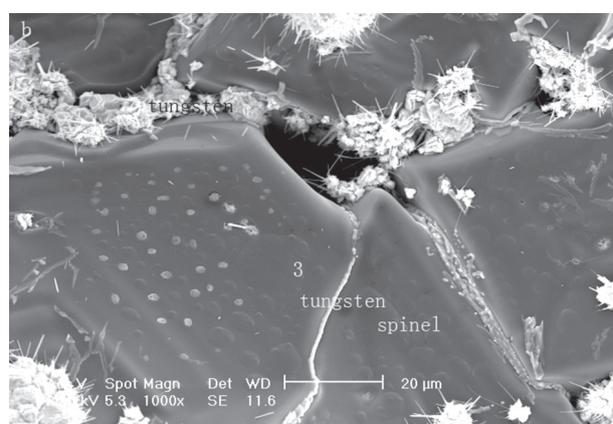
The morphology of tungsten is versatile, which was agglomerated or could be observed in the boundary of the spinel grains. Needle like residual WO_3 also can be found in Figure 5b. From Figure 5c, it was found that the tungsten was well crystallized and had a cubic structure with particle size of about 5-7µm.

DISCUSSION

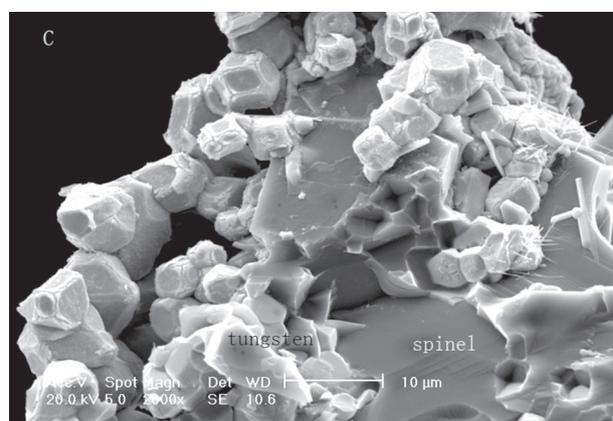
The unit cell of $MgAl_2O_4$ spinel can be stated as $Mg_8Al_{16}O_{32}$ in which the 32 oxygen anions are cubic close packed. Such close packing provides 64 divalent tetrahedrally coordinated cation sites and 32 octahedrally coordinated trivalent cation sites. In these cation sites, only one eighth of the tetrahedral sites are occupied by Mg^{2+} cations and half of the octahedral sites are filled by Al^{3+} cations. Thereafter, the unit cell of $MgAl_2O_4$ can hold a great deal of divalent and trivalent cations in solid solution. According to the phase diagram of the binary MgO - Al_2O_3 system, $MgAl_2O_4$ spinel is the only phase formed at temperature up to 1600°C [24]. The stoichiometric $MgAl_2O_4$ contains 28.2wt % MgO and 71.8 wt% Al_2O_3 . At this temperature, the solid solubility of MgO and Al_2O_3 in spinel is 2 wt.% and 6 wt.%,



a) 0 mol



b) 1.4 mol



c) 2.1 mol

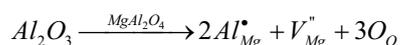
Figure 5. SEM micrographs of $MgAl_2O_4$ -W composite with 0, 1.4, 2.1 mol white fused corundum.

Table 1. EDS results of the points in Figure 5.

$Al_2O_3:MgO$		stoichiometric	1	2	3
Calculated	Mass ratio	71.8:28.2	71.8:28.2	77.5:22.5	88.8:11.2
	Molar ratio	1:1	1:1	1.35	3.11
Measured	Mass ratio	71.8:28.2	86.6:13.4	90.2:9.8	94.6:5.4
	Molar ratio	1:1	2.53	3.61	6.87

respectively. On increasing the temperature to 1700°C, the solubility in spinel increases to 3 wt.% and 10 wt.%, respectively. At 2000°C, the solubility of Al₂O₃ will exceed 20 wt.%. In site of the rapidly converging solvus lines with decreasing temperature in the phase diagram, the spinel structure can be easily sustain during cooling to ambient temperature for Al₂O₃ content up to 90%. At this time n = 3.5 if the composition of spinel is written as MgO · nAl₂O₃. Many authors has obtained different results of the limit solubility of the Al₂O₃, but the latest literature reported the solubility of the Al₂O₃ in MgAl₂O₄ spinel will reaches to 22 wt.% that is to say the n value is 7. So it is evident that on the Al₂O₃ rich side, n goes from n = 1 to n = 7 [25-30].

The structure of alumina rich spinel is a solid solution with crystal lattice defects because of the displacement of Mg²⁺ ion by Al³⁺. Yamamura and Masanobu Ezoé have indicated that the more alumina dissolved, the more defects formed, the less the lattice parameter and thermal expansion coefficient is [3,7]. On the contrary, the more magnesia solutes, the more lattice parameter and thermal expansion efficient are. In non-stoichiometric MgAl₂O₄ spinel, the divalent Mg²⁺ cations are substituted for trivalent Al³⁺ cations by the formation of cation vacancies deficiency. The deficiency equation can be written as:



where Kroger-Vink notation has been used. Here it is assumed that the vacancies occupy the tetrahedral sites. Though T. E. Mitchell et al indicated that vacancies could occupy the octahedral sites [31]. So the fractional concentration of the cation vacancies is related with the solubility of the Al₂O₃. From the previous discussions, it seems that the limit solubility of Al₂O₃ has been reached.

The cation vacancy is why the alumina rich spinel has good slag resistance. Because the cation vacancy can capture FeO of molten slag and increase the viscosity of the slag, so refractories contained a quantity of spinel, especially alumina rich spinel, will has good slag resistance. Furthermore, it can reduce the thermal expansion coefficient of the material and reduce the peeling, improve the thermal spalling stability. It is the key why alumina-magnesia castable containing alumina rich spinel, no matter how the spinel was added directly or in situ formed during the heat treatment.

The solid solution phenomenon only happens at higher temperature, it is very difficult to produce spinel at low temperature, more difficult to synthesize alumina rich spinel. Because the aluminothermic reaction is an extreme exothermal reaction, the system can reach very higher temperature, which makes the formation and growth of crystal more easily. So well crystallized and high solubility spinel can be produced using the high exothermic heats. Furthermore, because the reaction take place finish rapidly, so the soluted Al₂O₃ into the spinel is difficult to precipitation. From the XRD results, it can be

seen that the XRD peaks of corundum can't be detected, added white fused corundum has been dissolved into spinel and no exsolution happens.

The thermal expansion coefficient match is an important condition to prepare composite. Otherwise, extra thermal stress will lead to the formation of micro cracks and reduce the mechanical properties. Tungsten and spinel not only has perfect properties, but also the variance of expansion coefficient (the former is 5.5×10⁻⁶/K, the latter is 7.6×10⁻⁶/K) is not so big. At the same time, the expansion coefficient reduces with the rising of solution content of alumina. Thus the composite can be applied in some key parts, for examples, protection tube of apparatus for measuring temperature, injection nozzle, slide gates, and so on.

CONCLUSIONS

From the above discussion, we can get the following conclusions:

1. MgAl₂O₄/W composite can be easily obtained by aluminothermic method at low temperature. Spinel and tungsten are the main phases.
2. Alumina rich spinel with a high solubility of alumina was easily formed because of the high exothermic heats. The solubility limit of Al₂O₃ has reached when the content of Al₂O₃ is 2.1 mol.
3. The lattice parameter of spinel increases with the increment of the Al₂O₃ content. The rising of temperature can prompt the solution.

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