Reactive Andalusite: Properties and Application in Refractory Castable

X.-Y. Xiong, A. Derasse, M. Weissenbacher

It is very important to use a middle temperature (around 1000 °C) formed ceramic bonding that could work at high temperature (more than 1500 °C) for high performance refractories and ceramics. Damrec develops a new reactive bonding material starting from andalusite. A comparative reactivity study between this reactive andalusite and one typical reactive alumina is made in this research work. The results show that the ceramic bonding from reactive andalusite starts around 950 °C.

The origin of reactive andalusite formed ceramic bonding is following:

- mullitisation of reactive andalusite from 950 °C giving silica glass on the surface of mullite-andalusite
- merge of the silica glass each together: silica bonding
- secondary mullite formation between the silica glass and the fine alumina: mullite bonding.

The trial of applying this reactive andalusite in LCC refractory castable has been done. For castables with microsilica addition (3–5 %), reactive andalusite develops the same level bonding strength as reactive alumina from middle temperature to high temperature.

For free and very few microsilica castables, in middle temperature, the ceramic bonding created by reactive andalusite has the same level of strength than ceramic bonding due to reactive alumina. But in high temperature, reactive andalusite develops a stronger bonding by creating a complementary ceramic bonding by a secondary mullite formation between the glass phase on the surface of andalusite-mullite and calcined alumina.

1 Introduction

The chemical composition of andalusite is bioxides of aluminium and silicon: $Al_2O_3{\cdot}SiO_2$. Andalusite can be directly used as raw refractory material without any thermal treatment. Andalusite can be transformed to mullite (87,6 %) and silica glass (12,4 %) at 1000–1400 °C depending on the grain size. The following shows this thermal transformation process:

$$3(Al_2O_3{\cdot}SiO_2) \rightarrow 3Al_2O_3{\cdot}2SiO_2 + SiO_2$$

andalusite mullite glass

During mullitisation of the andalusite, the excess of SiO_2 is transformed to silica glass. The majority of this glass is trapped inside the mullite phase, while a small part of this glass is on the surface of the mullite crystal (Fig. 1) [1]. From middle temperature (1000 °C), the glassy phase softens inside the mullite, which allows the absorption of the stress due to the volume change of the mullite with the temperature change. In this way, the mullite transformed from andalusite has more thermal stability than other types of mullite. The glassy phase on the surface of andalusite-mullite crystal will bond the andalusite-mullite crystals. This glassy phase will react with reactive and calcined alumina to form a secondary mullite that bonds the andalusite-mullite crystal and alumina crystal.

Damrec is developing the reactive andalusite with D_{50} = 1–3 µm for ceramic bonding (refractory matrix) application. In this article, the reactive property of one of reactive

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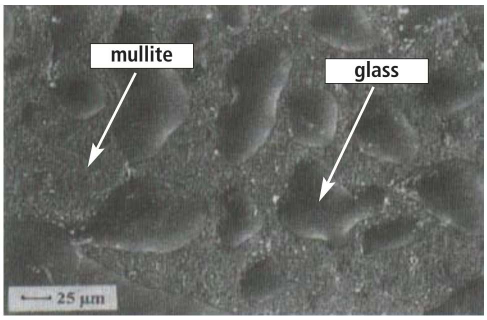

Fig. 1 Surface of andalusite after mullitisation

Tab. 1 Size and specific surface of Rad and RA

	Reactive andalusite Rad	Reactive alumina RA
D10 [µm]	0,72	0,28
D50 [µm]	1,37	0,93
D90 [µm]	2,53	2,81
BET [m^2/g]	18,265	6,551

andalusites in comparison with a typical reactive alumina, and the mechanic strength of the reactive Andalusite added Low cement content (LCC) castable in comparison with reactive alumina added castable are studied.

2 Property of reactive andalusite

2.1 Physico-chemical property

Reactive andalusite Rad (Al_2O_3: 60 %) is produced from Damrec's South Africa andalusite. A top level commercial reactive alumina RA (Al_2O_3: 99,9 %) is used for comparison.

Tab. 1 shows the size distributions of these two materials and the specific surface (BET) of reactive andalusite and reactive alumina.

The specific surface of reactive andalusite is more important than reactive alumina, which has a smaller particle size than reactive andalusite. That means reactive andalusite surface is rougher than reactive alumina.

2.2 Sinter reactivity

The samples for sintering were prepared by a press in a mould with a pressure of 1000 kg/cm^2 without any additive. The size of sample is 50 mm × 10 mm × 12 mm. The sintering tests were carried out to compare the reactivity of reactive andalusite and that of reactive alumina. A shrinkage and a mechanical strengthened phenomenon accompany the sintering process of a mineral material. We determine the shrinkage Permanent Linear Change (PLC) and Cold Module Of Rupture (CMOR) of sample.

The samples were sintered at different temperatures starting from 700 °C up to 1500 °C at temperature interval steps of 50 °C. The firing rate was taken from the EN 1402-5 (common castable) and holding time was 3 h.

The figures represent the shrinkage (Fig. 2) and the cold module of rupture (Fig. 3) of the samples made of reactive andalusite (Rad) and reactive alumina (RA).

One can see clearly the PLC and CMOR increase evidently around 950 °C for reactive andalusite, and around 1100 °C for reactive alumina. This means the beginning of sintering of reactive andalusite and reactive alumina.

One can follow the mineralogical evolution of the sample of reactive andalusite from 700 °C to 1500 °C. Fig. 4 illustrates the mullitisation depth with temperature.

The mullitisation of reactive andalusite starts around 950 °C and ends around 1350 °C. The beginning of mullitisation of this reactive andalusite is 200 °C lower than that of the normal andalusite. This indicates the possibility of creation of ceramic bonding from reactive andalusite should start around 950 °C. The correspondence between the beginning temperature of sintering process and the beginning temperature of mullitisation indicates that origin of sintering is the coalescence each other of glassy phase on the surface of nearby andalusite-mullite – consequence of mullitisation of andalusite. After complete mullitisation of reactive andalusite around 1350 °C, the sample continues to shrink. This is due to decrease of porosity of sample (crystal rearranging or growing). The reactive alumina shrinkage starts around 1100 °C. This means the beginning of reaction of ceramic bonding by crystal growth. We can find the same beginning temperature for increasing the CMOR.

One can conclude the beginning of creation of ceramic bonding of reactive andalusite is 150 °C earlier than reactive alumina.

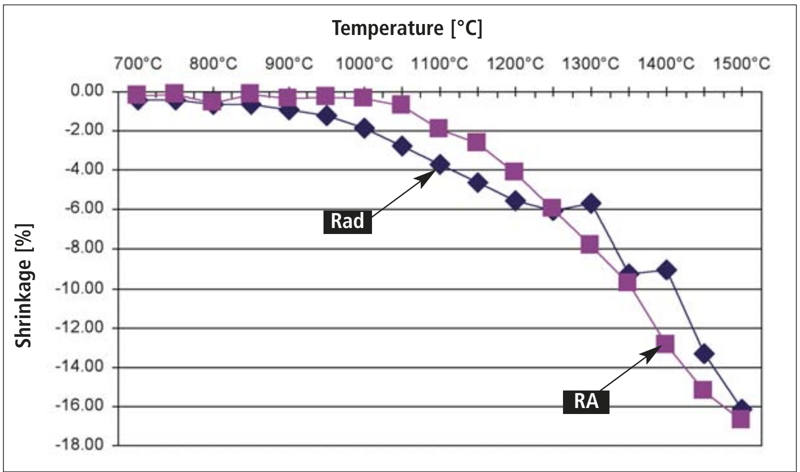

Fig. 2 Sintering shrinkage of sample

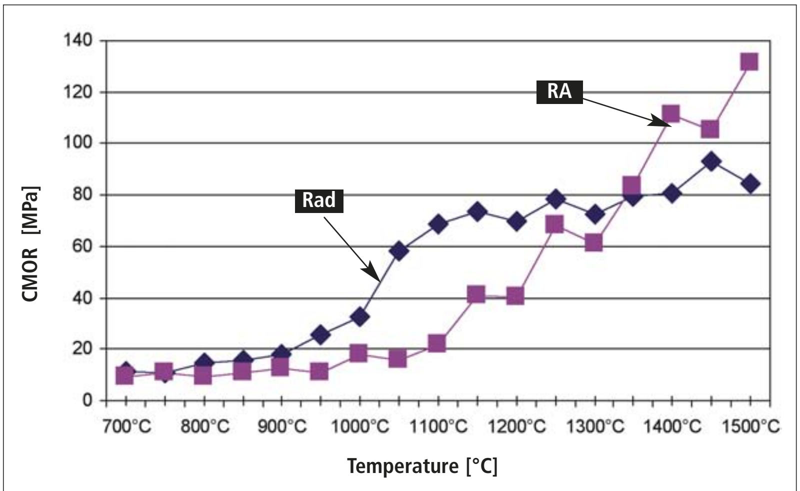

Fig. 3 CMOR of sample

3 Application in refractory castable

3.1 Formulation of castable

Four castables were used to test the reactive andalusite in substituting reactive alumina: a white fused alumina castable without microsilica addition (steel ladle wall lining), a spinel castable with a few (0,3 %) microsilica addition (steel ladle bottom lining), a bauxite castable with 5 % microsilica addition (blast furnace iron trough) and a SiC castable with 3 % microsilica (blast furnace main trough). Tab. 2 shows the composition of these castable in two versions: reactive alumina version (form RA) and reactive andalusite version (form Rad). The water addition is 5,5 % for all castable.

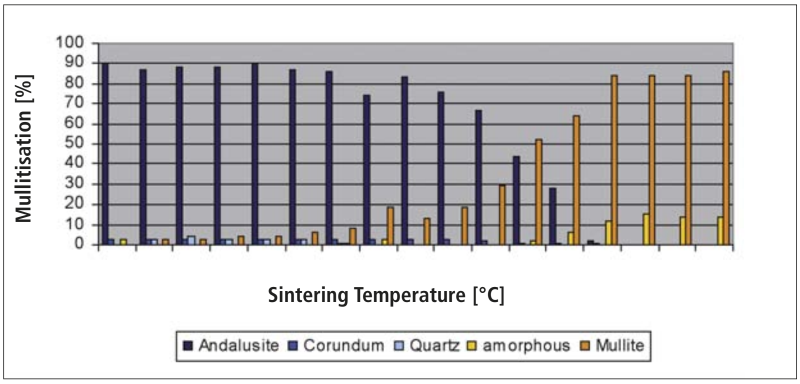

Fig. 4 Mineralogical evolution of Rad

3.2 Casting property

The substitution of reactive alumina by reactive andalusite has no effect on working ability (water addition, flow ability and setting time) of castable. Figs. 5, 6 show the open porosity and density of castable sample after drying at 110 °C for 24 h.

One can see the open porosities stay at the merely same results from reactive alumina castable to reactive andalusite castable. The

Tab. 2 Composition of castable to test

Raw materials	Size	WFA castable		Spinel castable		Bauxite castable		SiC castable	
		form RA [%]	form Rad [%]	form RA [%]	form Rad [%]	form RA [%]	form Rad [%]	form RA [%]	form Rad [%]
white fused alumina	5–10 mm			15	15				
	2–5 mm	33	33	20	20				
	1–3 mm	10	10	20	20				
	0–1 mm	20	20	10	10				
	0–0,3 mm	15	15					3	3
brown fused alumina	5–10 mm							14	14
	3–5 mm							20	20
	1–3 mm							22	22
	0–1 mm							5	5
tabular alumina	325M							2	2
sinter spinel 78 %	0–0,5 mm			5	5				
	325M			14	14				
bauxite 88 %	3–5 mm					16	16		
	1–3 mm					20	20		
	0–1 mm					24	24		
	200M					20	20		
SiC 97 %	100M							6	6
	200M							14,4	14,4
black carbon								0,3	0,3
B4C	30 µm							0,15	0,15
microsilica	971U			0,5	0,5	5	5	3	3
calcined alumina	5 µm	11	11	5	5	5	5	3	3
reactive alumina	**1 µm**	**6**		**6**		**5**		**4**	
reactive andalusite	**1 µm**		**6**		**6**		**5**		**4**
cement	secar 71	5	5	5	5	5	5	3	3
STPP		0,15	0,15	0,15	0,15	0,15	0,15	0,15	0,15
total		**100,15**	**100,15**	**100,65**	**100,65**	**100,15**	**100,15**	**100**	**100**
water addition		**5,5**	**5,5**	**5,5**	**5,5**	**5,5**	**5,5**	**5,5**	**5,5**

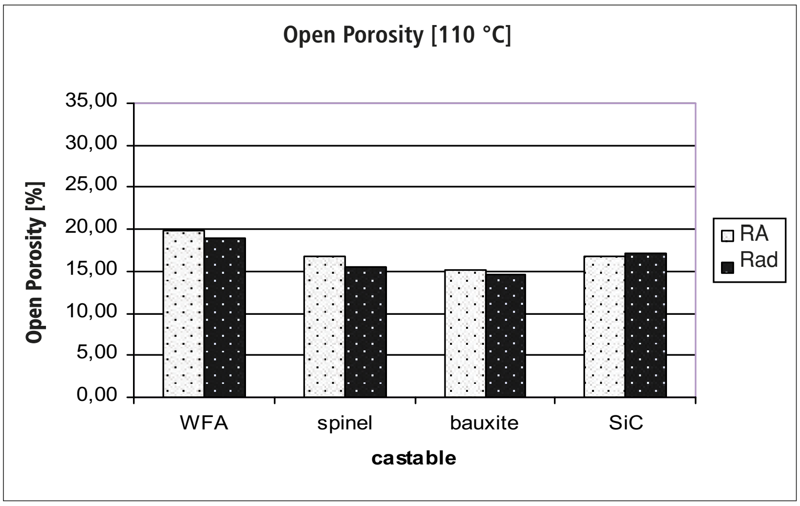

Fig. 5 Porosity of castable

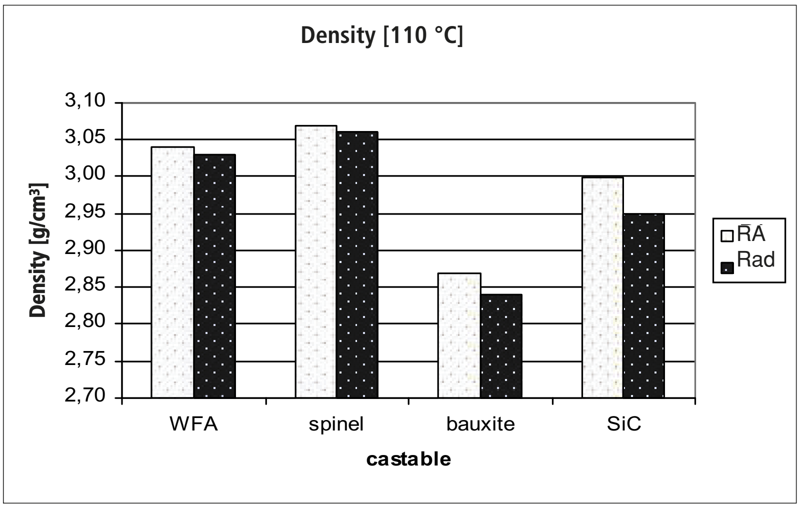

Fig. 6 Density of castable

densities of reactive andalusite castable are lightly lower than the reactive alumina castables. This is due to the lower density of reactive andalusite regarding the density of reactive alumina. All means the substitution of reactive alumina by reactive andalusite has no impact on casting quality of castable.

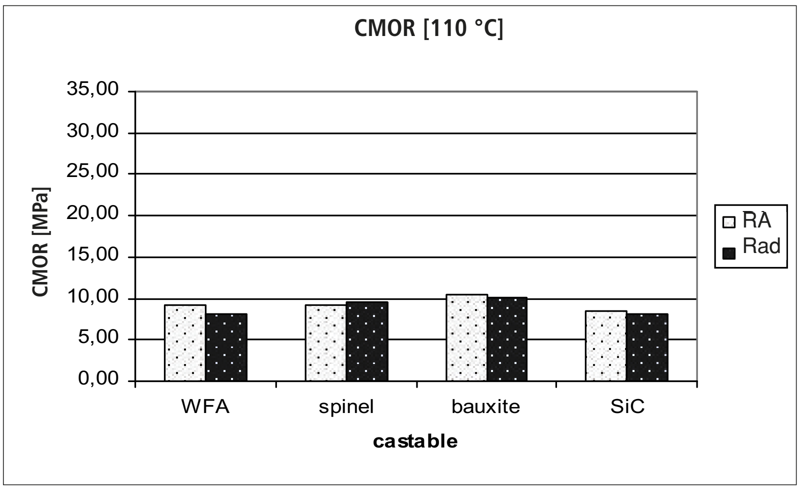

Fig. 7 CMOR [110 °C] of castable

3.3 Mechanical strength

The mechanical strength of the castable was determined by measuring its CMOR. Figs. 7–9 summarize the CMOR for 110 °C, 1000 °C and 1500 °C of four castables:

For 110 °C, the CMOR values (Fig. 7) have quite same value between the reactive alumina castable and the reactive andalusite castable. These correspond to the above working ability results.

At middle temperature 1000 °C (Fig. 8), for the castables without microsilica (WFA castable) and with few microsilica (Spinel castable), the reactive andalusite develops a lightly stronger bonding than the reactive alumina (the CMOR of reactive andalusite castable are higher than the reactive alumina castable). This means the glass bonding due to merge between glassy on the surface of reactive andalusite is stronger than the bonding formed by reactive alumina. For the castables with microsilica (bauxite castable and SiC castable), the CMOR of reactive alumina castable are lightly higher than reactive andalusite castable. The reason may be following: in reactive alumina castables, the soften microsilica powders merge each other (glass bonding) and react with reactive alumina to form a complementary mullite bonding. The consolidation of these two bondings of reactive alumina castable with microsilica are more stronger than the merge between soften microsilicas and glass on surface of reactive andalusite in reactive andalusite castable.

At high temperature 1500 °C (Fig. 9), the situations of two castables with microsilica stay in same as middle temperature. But for two castable with free and few microsilica, the two reactive andalusite castables develop the much stronger CMOR than two reactive alumina castable. We can explain that as following: in reactive andalusite castables, the calcined alumina reacts with glass on the surface of mullite-andalusite to form a mullite bonding, and in reactive alumina castables, the only bonding is from sintering between reactive alumina powders.

3.4 Effect of microsilica

Figs. 10–11 show the evolution of CMOR in function of the temperature. For the reactive alumina castable (Fig. 10), microsilica is necessary to develop a stronger bonding at high temperature.

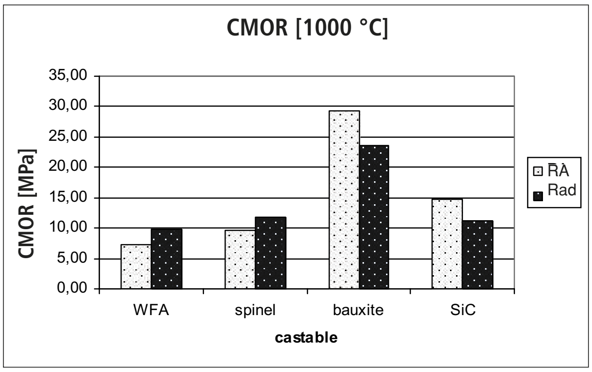

Fig. 8 CMOR [1000 °C] of castable

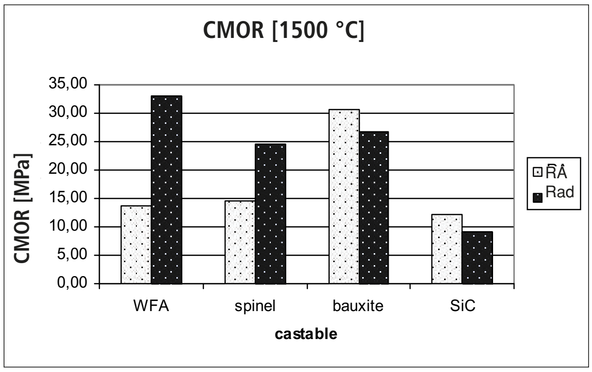

Fig. 9 CMOR [1500 °C] of castable

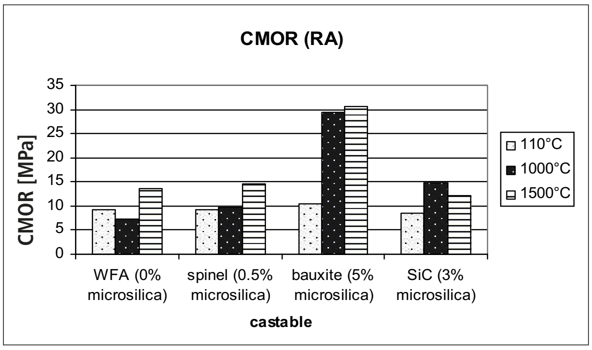

Fig. 10 Microsilica effect on castable

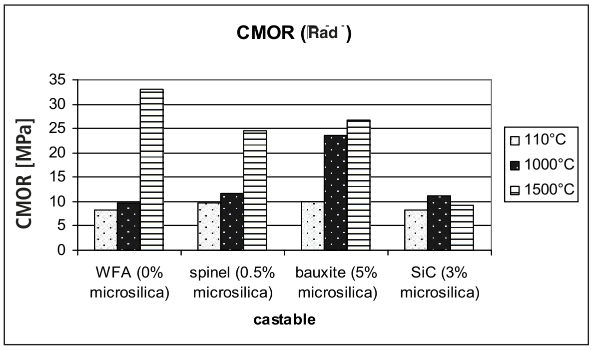

Fig. 11 Microsilica effect on castable

For reactive andalusite castable (Fig. 11), the addition of microsilica develop a stronger bonding since medium temperature as reactive alumina castable. For the castables without microsilica or very little microsilica, reactive andalusite develops a very stronger bonding at high temperature (from 1250 °C [2]). This means the possibility to substitute microsilica by reactive andalusite for strengthening mechanically the LCC and ULCC castable.

Due to carbon content, two SiC castables have the lower mechanical strength bonding for all temperature.

4 Conclusions

The reactive andalusite starts its mullitisation around 950 °C and ends around 1350 °C. Starting temperature of ceramic bonding formation by reactive andalusite is 150–200 °C below starting temperature for creating a ceramic bonding with reactive alumina.

For castables with microsilica addition (3–5 %), reactive andalusite develops the same level bonding strength as reactive alumina from middle temperature to high temperature.

For free and very few microsilica castables, in middle temperature (800–1200 °C), the ceramic bonding created by reactive andalusite has the same level of strength than ceramic bonding due to reactive alumina. But in high temperature, reactive andalusite develops a stronger bonding by creating a complementary ceramic bonding by a secondary mullite formation between the glass phase on the surface of andalusite-mullite and calcined alumina. Without microsilica addition, reactive alumina castable doesn't develop a stronger bonding. This means it's possible to substitute reactive alumina and microsilica together by reactive andalusite in some type of castable.

References

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