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CARBONIZATION OF PITCH AND RESIN AS CARBON-BOND ADDITIVES IN CEMENTLESS CASTING REFRACTORIES

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ABSTRACT

As carbon-bond additives in cement-less casting refractories, the carbonization behaviour of various pitches and resins, as well as their mixtures are experimentally studied by examining the carbonization degree with residual weight, the graphitization degree with XRD, the microstructure with SEM and the anti-oxidation capability with DTA, arriving at the conclusion that the mixture of 65%pitch-35%resin is the best carbon-bond additive for cement-less casting refractories.

1. INTRODUCTION

Owing to the non-wetting characteristics of carbon by molten slags and metals, carbon-containing Al_2O_3-SiC-C refractories have excellent properties of anti-erosion by slag and metal melts, and thus have been widely used as linings of metallurgical vessels and troughs. Being castable, cement bonded Al_2O_3-SiC-C casting refractories have been vastly used for blast furnace runners. But, the presence of cement in the materials is unfavourable to their performance because of eutectic formation to lower materials fireproofness, water addition to loosen materials structure upon drying, and hydration of metal (e.g. Al) powder additions. Therefore, applying carbon-bond in stead of cement-bond, the development of low cement, or even cement-less castable Al_2O_3-SiC-C refractories is of great practical significance. To form carbon bond in casting refractories, pitches and resins are usually used. The objective of the present work is thus to find the optimum pitch, resin or their mixture.

2. EXPERIMENTS

Weigh a certain quantity of pitch, putting it into a ceramic crucible. Heating the sample with 2℃/min to 800℃ under N_2 atmosphere. Holding for 1 hour and then cooling slowly to room temperature. The carbonization degree is determined by weighing the sample. The layer gap of carbon ($d00_2$) is determined by XRD, which reflects the graphitization degree. The microstructure is determined by SEM, and the anti-oxidation capability is determined by DTA.

For the carbonization of pitch-resin mixtures, in addition to the above analyses, the micro-strength-index (MSI) of the carbonized mixture is measured as follows. Together with steel balls, carbonized samples are put into a stainless steel tube. The tube is then rotated at 25 rpm for 32 min. After revolution, the sample is sieved and the weight percentage of +65 mesh is defined as MSI.

3. RESULTS AND DISCUSSION

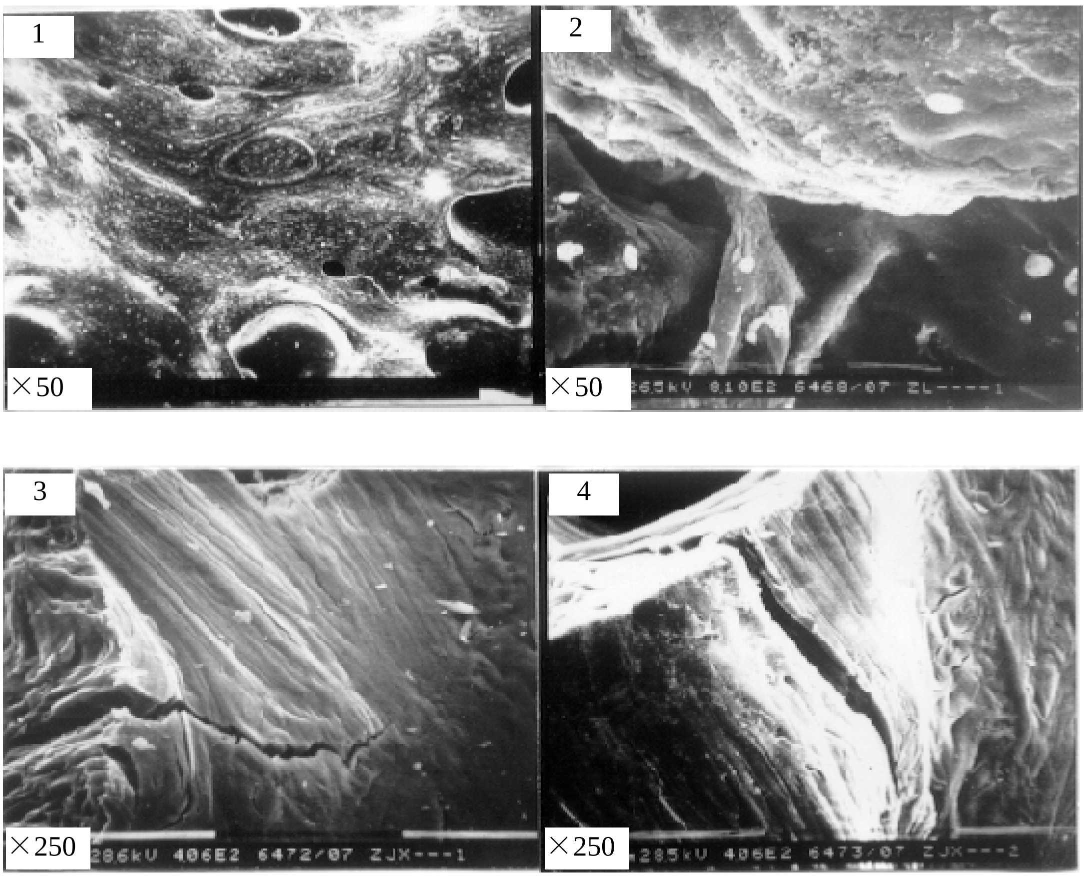
The carbonization degrees and properties of carbonized pitch samples are listed in Table 1. From the table one can see that, the higher the β-resin (BI-QS, where BI and QS denote benzene-insoluble and quinoline-soluble respectively) and the higher the quinoline-insoluble

(QI) are, the higher is the carbonization degree. The interim-phase pitch is already in the state of transition from liquid to solid.

Table 1 Carbonization degree and properties of different pitches

Sample	BI, %	QI, %	β, %	Carbonization degree, %	doo_2, Å	DTA, ℃
Middle temp. pitch (MT)	20	4	16	51.94	3.531	585
High temp. pitch (HT)	17	3.9	13.1	56.43	3.481	675
Fine pitch (F)	34.95	11.2	23.75	71.95	3.451	
Taigang pitch (TG)	24.53	8.49	16.04	58.43	3.478	
Interim-phase pitch (IP)	82.74	39.96	42.98	79.02	3.4636	690
MT + 5%IP	26.27	7.58	18.7	54.42		
MT + 10%IP	32.55	11.15	21.4	56.17		
Zhenjiang pitch	25-28	2.5-3.5	23-25	63.44	3.4876	528
Luoyang pitch	28	7.8	20.2	58.36	3.4716	528

The microstructures of carbonized pitches are shown in Figure 1. From the figures one can see that the micro morphologies of all the carbonized pitches are in flowing states.



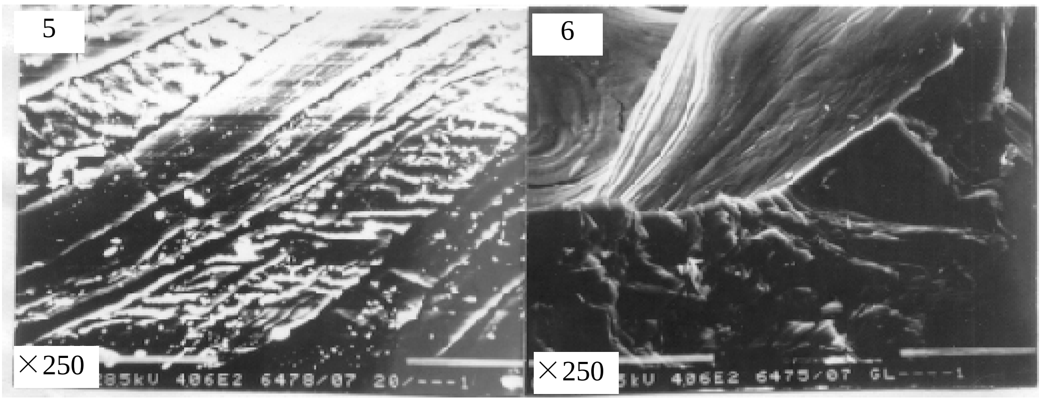


Figure 1 SEM photographs of carbonized pitches

1, 2 —MT pitch 3, 4 —IP pitch 5 —MT + 10%IP 6 —HT pitch

The XRD curves of a few carbonized pitches are shown in Figure 2. The carbonization product of pitch is of easy-graphitization carbon. Because of the low carbonization temperature, however, the layer gap of the carbon crystals is relatively big.

The DTA curves of a few carbonized pitches are shown in Figure 3. From the figures one

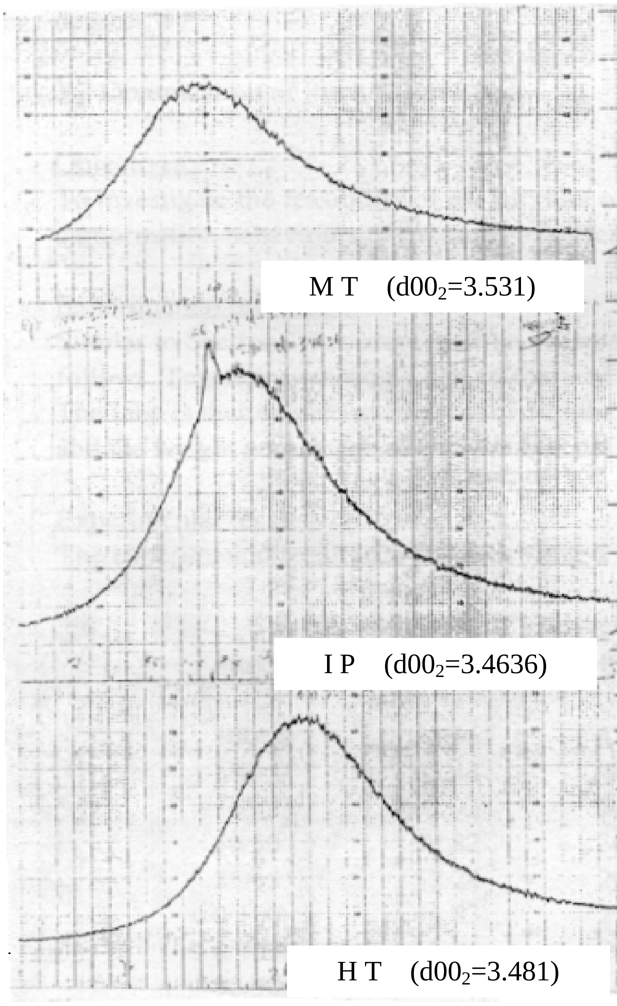


Figure 2 XRD curves of carbonized pitches

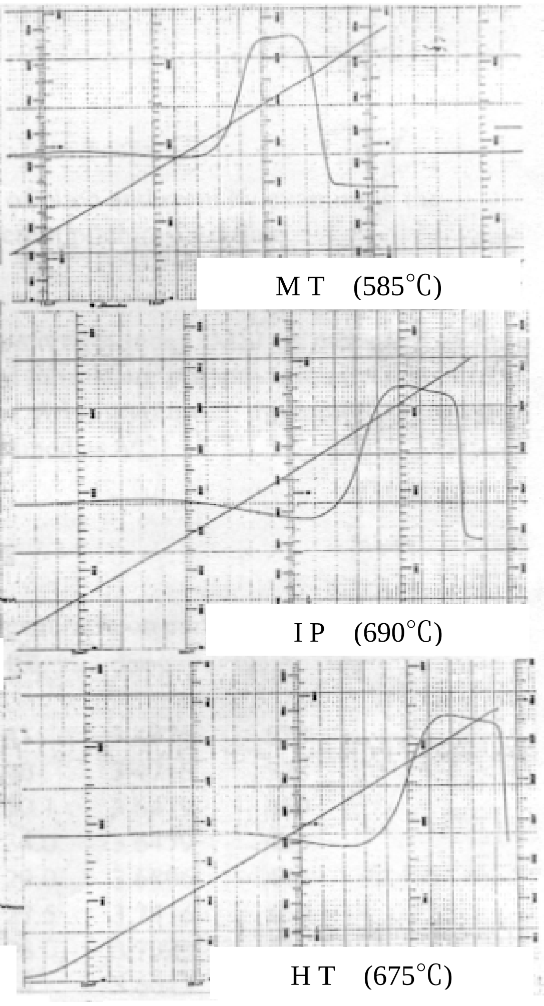


Figure 3 DTA curves of carbonized pitches

can see that the temperatures of starting oxidation of carbonized MT, HT and IP pitches are in correspondence with their graphitization degrees, i.e. the higher the graphitization degree is, the more stable is the structure, and therefore the better is the anti-oxidation property.

From the above discussion on carbonized pitches, we can get the following conclusions. The micro morphologies of carbonized pitches are all of flow structures. The carbonization degree increases with increasing the β-resin and QI contents in pitch. The anti-oxidation capability of carbonized pitches is in correspondence with its graphitization degree.

The feasibility of use mixture of pitch and resin was investigated, the carbonization degrees and properties of carbonized pitch-resin mixtures are listed in Table 2.

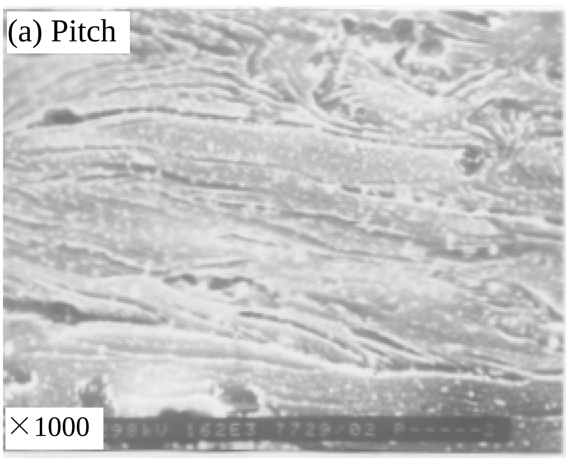
Table 2 Influence of pitch/resin ratio on carbonization

Pitch/resin	Carbonization degree, %	MSI, %	d_{002}, Å	DTA, ℃
100*/0	58.36	41	3.4876	528
100 /0	63.44	40	3.4716	528
65/35	62.92	50.1	3.6479	450
50/50	59.82	34.0	3.6479	455
35/65	57.24	29.0	3.6806	445
0/100	44.83	27.5	3.7416	460
0/100(L)**	51.75	28.0	3.7323	475
50/50(L)	59.14	44	3.6043	465

* Zhenjiang pitch. All others being Luoyang pitch.

** Liquid resin. All others being powder resin.

The SEM photographs ofcarbonized samples are shown in Figure 4. From the figures one can see that micro morphology of carbonized pitch is of flowing structure (Figure 4a), while that of carbonized resin is of glass structure (Figure 4b, c). The micro morphology of carbonized pitch/resin mixture is of fine andinterlink structure (Fig. 4d, e), which is favourable to strength.



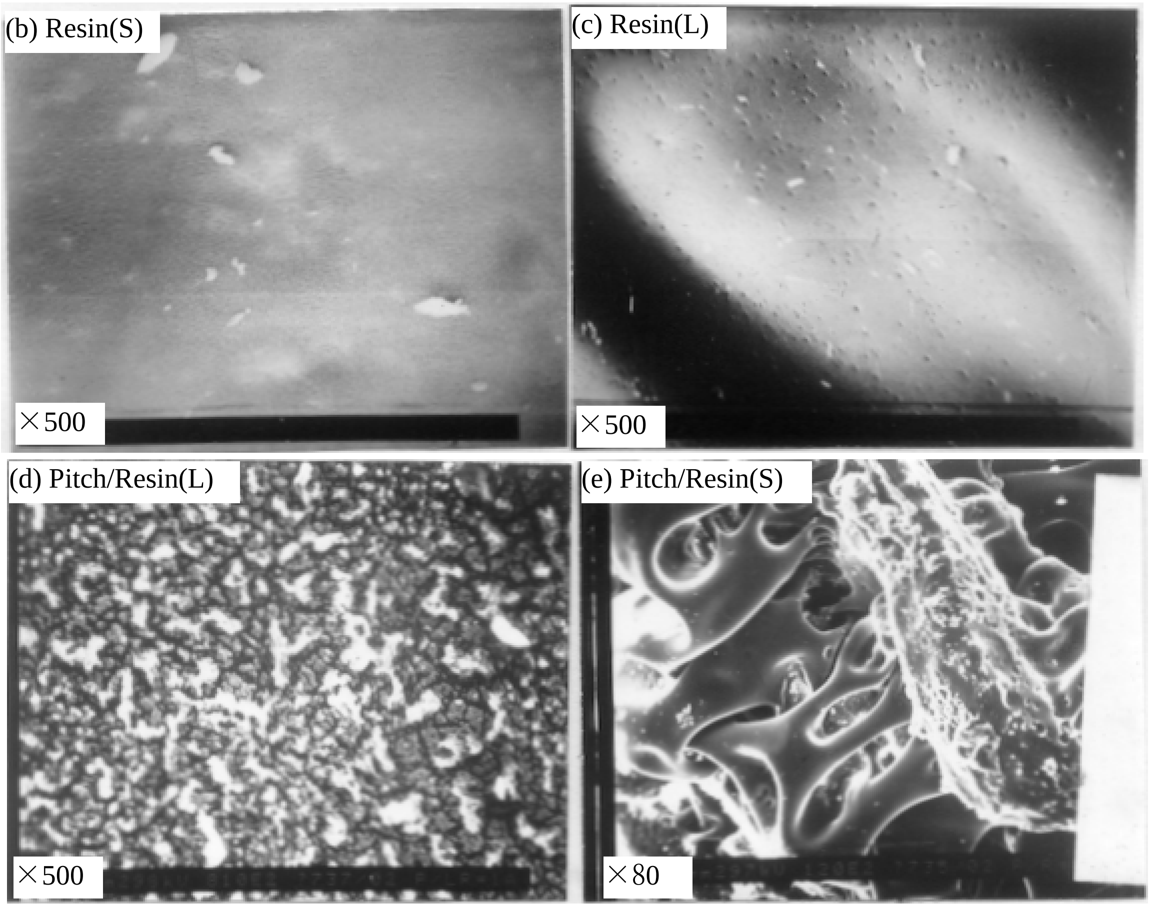


Figure 4 SEM photographs of carbonized samples

The carbonization degrees of all pitches are higher than that of resin (no matter solid or liquid). For pitch-resin mixtures, the carbonization degree decreases with increasing resin proportion as shown in Figure 5. Since the MSI indicates directly the abrasive resistance, it reflects indirectly the structure strength. As shown in Figure 6, suitable pitch-resin ratio is favourable to the strength of carbonized pitch-resin mixture.

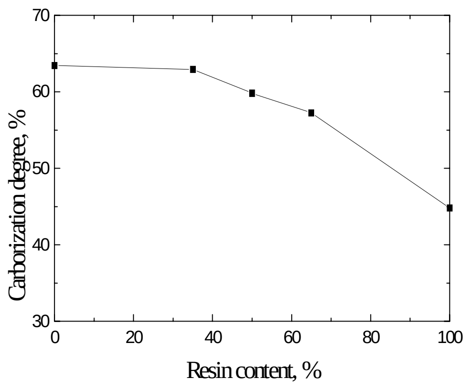


Figure 5 Influence of resin content on carbonization degree

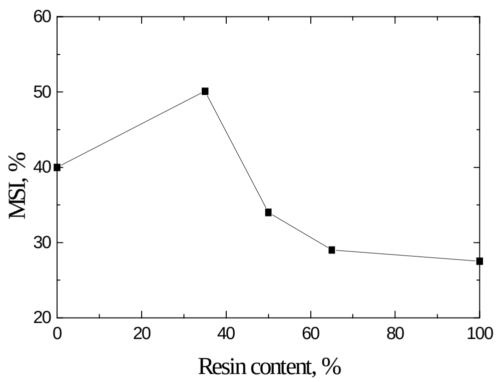


Figure 6 Influence of resin content on MSI

The XRD curves for carbonized pitch, resin and their mixtures are shown in Figure 7. From the figures one can see that the graphitization degree of carbonized pitch is higher than that of resin. For pitch-resin mixtures, the graphitization degree decreases with increasing resin content.

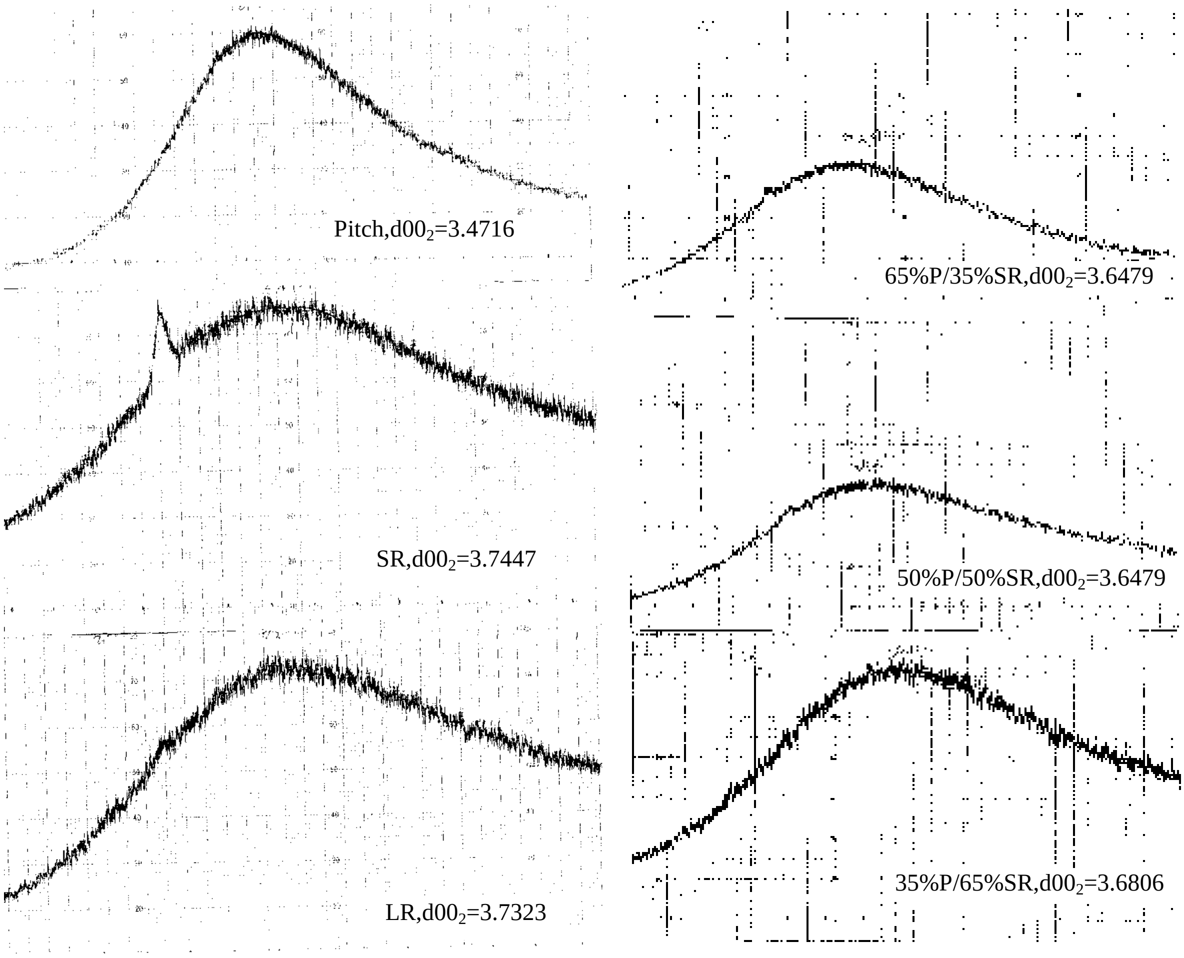


Figure 7 XRD curves for carbonized pitch, resin and their mixtures

The DTA curves for carbonized pitch, resin and their mixtures are shown in Figure 8. From the figures one can see that the temperature of starting oxidation of carbonized resin is lower than that of pitch. The thinner picks of resins' curves show that the oxidation is quicker that that of pitch. For pitch-resin mixtures, the temperature of starting oxidation decreases with increasing the content of resin.

From the above experimental results, we can get the following conclusions. The micro morphology of carbonized pitch-resin mixture is of fine interlink structure, which is favourable to strength. With increasing the content of resin, however, all carbonization degree, graphitization degree and anti-oxidation ability tend to decrease.

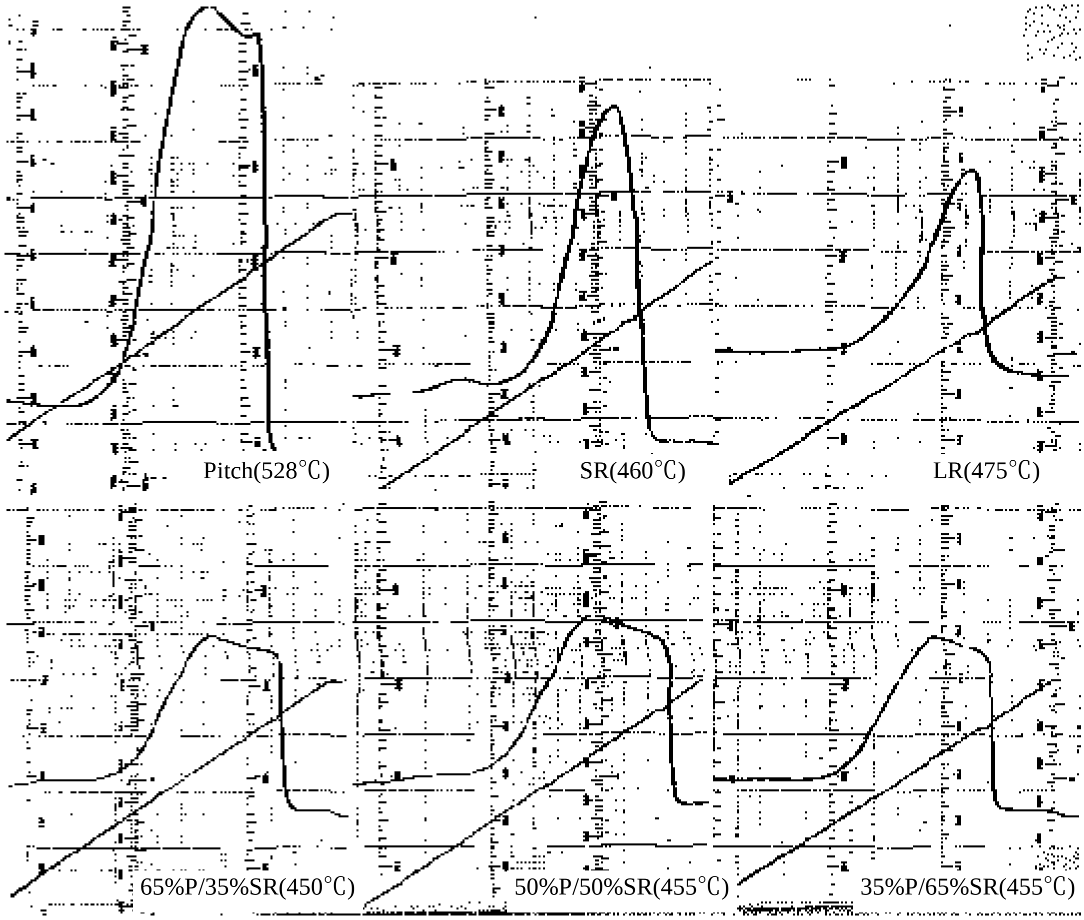


Figure 8 DTA curves for carbonized pitch, resin and their mixtures

3. CONCLUSION

Considering both carbonization degree and the strength of the carbonized product, mixtures of about 65%pitch-35%resin are the best selection as carbon-bond additives for cementless casting refractories.