

MICRO-RAMAN SPECTRA RESEARCH ON NaF-AlF₃-NaCl MELTS

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Abstract

Raman spectra of NaF-AlF₃-NaCl melts with the compositions in aluminum electrolysis practice are recorded by using the ultraviolet laser source. A kind of sealed sample cell was used to improve the measuring precision. The ionic structure of the melts with different cryolite ratio (molar ratio between NaF and AlF₃) and NaCl contents was studied. The effect of the composition and temperature was analyzed. The results show that with the addition of the NaCl to the acidic NaF-AlF₃ melts, the relative contents of the Al-F entities have been changed greatly. It is thought that the relative contents of the complex ions are also greatly influenced by the temperature.

Introduction

NaCl is a kind of cheap additives in modern aluminum electrolysis cells for its significant effect of decreasing the liquidus temperature and increasing the electrical conductivity of aluminum electrolyte. The ionic structure of aluminum electrolysis melts is closely related to the physicochemical properties and affects the electrode process.

Raman spectroscopy is an important method for the research on ionic structure of melts. There have been a lot of studies on the structure of aluminum electrolyte by Raman spectroscopy, and some of the additives are involved [1-4]. Tixhon [4] has studied the structure of NaF-AlF₃-NaCl melts with a wide content of NaCl. In his study, the macro-Raman spectrometer and a "windowless" sample cell are used.

Since the 1980s, micro-Raman technology has been developed rapidly for its advantage of high power density. On the other hand, the application of UV laser and pulsed laser has improved the development of the high temperature Raman spectroscopy. Furthermore, it is known that both molten fluorides and chlorides are strongly volatile at the temperatures of aluminum electrolysis. Therefore, if the sample cell is open, like the windowless cell, the experimental precision will be affected because the sample component may be changed caused by the volatilization.

In the present study, ionic structure of NaF-AlF₃-NaCl melts was studied by UV micro-Raman spectroscopy with the use of a closed sample cell. The effect of temperature and weighted-in composition are analyzed.

Experimental

AlF₃ was resublimed at 1050°C under vacuum, and other chemicals were dried at 300°C for 24h to remove attached water. 15g of mixture with the needed composition were premelted in a platinum crucible for well mixing. About 0.1g of cooled sample was taken for Raman spectra recording.

The heating furnace and the cell are shown in figure 1.

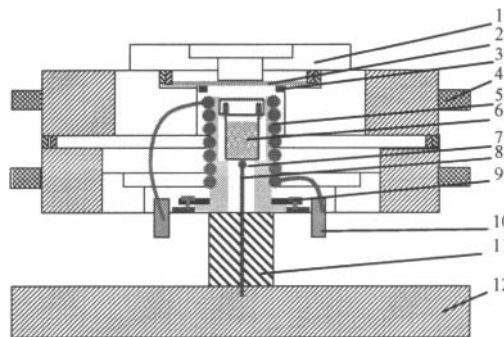


Figure 1. Construction of the heating furnace and sample cell
1-Furnace lid; 2- Quartz plate; 3-Washer; 4-Cooling water hole; 5-Platinum wire; 6-Sample cell; 7-Furnace hearth; 8-Thermo couple; 9-Gasket; 10-Terminal; 11-Pillar; 12-Base.

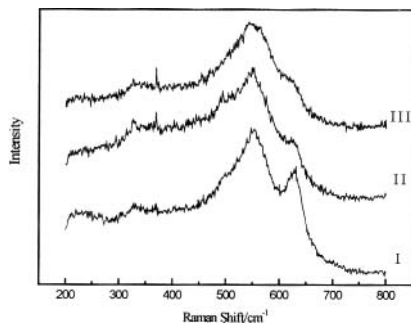
The base and pillar are made of copper and aluminum, respectively. The pillar is connected to the main body by the threaded connection. The main body contains two copper parts. They are connected by threaded connection and cooling water is flowing through in them. In the cavity of the main body, there is a corundum tube which has an external thread for the platinum wire wound around. The tube has two ledges for fixing itself on the inner bottom surface of the main body by using the screws. The inner diameter at the lower part of the tube is smaller than the higher part. Therefore the sample cell can be placed on the platform. The lid of the furnace is also made of copper. It is connected to the main body by the threaded connection too. There is a fovea in the lid, which inner diameter is bigger than the outer diameter of the Raman microscope lens. Therefore the lens can enter into the fovea to ensure that the distance between the lens and the sample is short enough for focusing.

As mentioned above, to avoid the effect of uneven volatilization of the melts, a closed sample cell is used. A platinum crucible ($\Phi 5 \times 6$) placing in the corundum tube was used as molten sample holder. A quartz lid with a ring groove was tightly coupled with the platinum crucible. The cell was sealed by the high-temperature cement. The lower surface is only about 1mm higher than the liquid sample, which ensures that the volatile will not be condensed on the lid because of the high temperature. A Guolong TCW-32B temperature controller connected to a Pt-PtRh₁₀ type thermocouple was used to controlling the temperature.

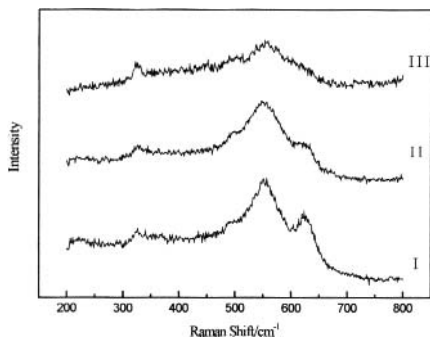
A Kimmon Koha He-Cd UV laser (18mW, 325.0nm) was used to generate the exciting laser and a Olympus UV microscope objective (10 \times 0.25) was used for observing the samples. Raman spectra were recorded by a Horiba Jobin Yvon Labram HR 800 Raman spectrometer with accumulating 15s for 2 times. No smoothing procedure has been applied to the spectra.

Results and discussion

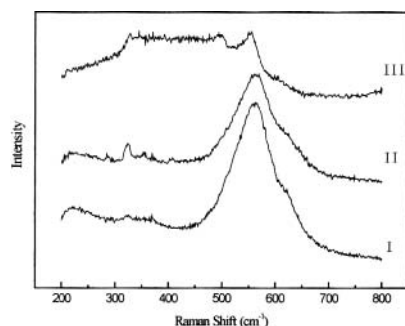
Raman spectra of NaF-AlF₃-NaCl melts with different molar ratio between NaF and AlF₃ and NaCl content at different temperature are shown in figure 2.



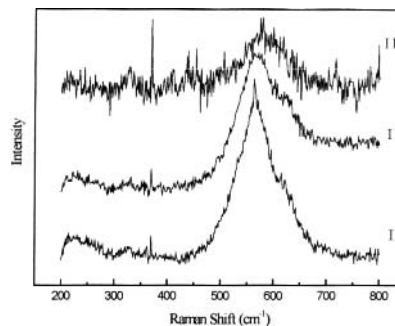
(a)



(b)



(c)



(d)

Figure 2 Raman spectra of NaF-AlF₃-NaCl melts

- (a) 2.3NaF-AlF₃-1wt%NaCl melts;
 - (b) 2.3NaF-AlF₃-2wt%NaCl melts;
 - (c) 2.7NaF-AlF₃-1wt%NaCl melts;
 - (d) 2.7NaF-AlF₃-2wt%NaCl melts.
- I. 1010°C; II. 1020°C; III. 1030°C.

It can be observed from the spectra shown in figure 2 that there is a strong peak located at about 555cm⁻¹, and at about 624cm⁻¹, there also is a peak with middle strength with some of them existing as the shoulder of the peak of 555cm⁻¹. In our previous research results [5], the peaks corresponding to the symmetric stretching vibration of AlF₄⁻ and AlF₆³⁻ are located at 622cm⁻¹ and 555cm⁻¹, respectively. From the similar Raman shift, it is thought that in the studied melts, AlF₄⁻ and AlF₆³⁻ exist in NaF-AlF₃-NaCl melts. In the spectra in figure 2, one can also see an obvious peak located at about 325cm⁻¹, which is thought to be caused by the deformation flexural vibration of AlF₄⁻ [6].

According to the discussion above, it seems that there is no new complex generated when NaCl is added to NaF-AlF₃ melts. Which conclusion is in agreement with the results of Tixhon [4]. However, in the spectra shown in figure 2(a), there is a weak peak located at about 500cm⁻¹, which seems similar to the value of 515cm⁻¹ appointed to the symmetric stretching vibration of AlF₆³⁻ in Gilbert's research results [7]. Meanwhile, the peak at 555cm⁻¹ was thought to be caused by the symmetric stretching vibration of AlF₅²⁻ in the same literature. But, in our scanned spectra of NaF-AlF₃ melts [5], there is no peak at about 515cm⁻¹. Therefore, it seems likely that the peak of 500cm⁻¹ is caused by some new complex containing Cl⁻. It may be some resultant of the substitution of F⁻ in Al-F complex by Cl⁻. The detailed structure need to be further studied.

In order to obtain the more detailed information about the vibration properties of ionic species, the related characteristic bands in the spectra should be fitted by some kind of equation to get the value of the maximal height of the peak, the position of the maximum and the bandwidth at half height. However, the effect of the blackbody emission should be removed by adjusting the baseline before the fitting. As for the fitting equation, it is generally thought that the Gauss equation or Lorentzian equation is reasonable. Many authors have claimed that the best fitting equation is the summation of the two curves. In the present study, the Raman band has been fitted by using the "Peak searching and fitting" option of Labspec software.

The fitted data of the related Raman characteristic peaks is shown in Table I. The intensity ratio stands for the ratio between the intensity of the present peak to that of the peak belong to AlF_6^{3-} . Some parameters are not obtained because of the poor quality of the spectra.

Table I The fitted data of the Raman peaks

(a) 2.3NaF-AlF ₃ -1wt%NaCl melts				
Peak Position	T(°C)	$\nu_{\max}(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	Intensity ratio
~555 cm^{-1}	1010	554	73	1
	1020	552	80	1
	1030	549	83	1
~624 cm^{-1}	1010	632	37	0.69
	1020	626	37	0.30
	1030	624	38	0.25
~500 cm^{-1}	1010	495	41	0.22
	1020	493	43	0.39
	1030	490	43	/
(b) 2.3NaF-AlF ₃ -2wt%NaCl melts				
Peak Position	T(°C)	$\nu_{\max}(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	Intensity ratio
~555 cm^{-1}	1010	554	63	1
	1020	552	70	1
	1030	550	72	1
~624 cm^{-1}	1010	627	38	0.60
	1020	625	40	0.34
	1030	613	40	0.32
~500 cm^{-1}	1010	496	15	0.11
	1020	491	30	0.25
	1030	499	41	0.42
(c) 2.7NaF-AlF ₃ -1wt%NaCl melts				
Peak Position	T(°C)	$\nu_{\max}(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	Intensity ratio
~555 cm^{-1}	1010	560	74	1
	1020	560	77	1
	1030	554	78	1
~624 cm^{-1}	1010	624	38	0.54
	1020	620	42	0.33
	1030	/	/	/
~500 cm^{-1}	1010	503	44	0.08
	1020	500	47	0.32
	1030	496	49	0.60
(d) 2.7NaF-AlF ₃ -2wt%NaCl melts				
Peak Position	T(°C)	$\nu_{\max}(\text{cm}^{-1})$	$\Delta\nu(\text{cm}^{-1})$	Intensity ratio
~555 cm^{-1}	1010	563	75	1
	1020	571	78	1
	1030	580	/	1
~624 cm^{-1}	1010	625	34	0.49
	1020	623	36	0.28
	1030	/	/	/
~500 cm^{-1}	1010	/	/	/
	1020	/	/	/
	1030	/	/	/

Observing the data in Table I, one can find the red-shift when the temperature increases for most of the characteristic peaks. Which is attracted to that higher temperature leads to looser structure. Meanwhile, the width of peaks increases with the temperature. That means that the structure is more unstable at higher temperature. Comparing the relative intensity of the peaks of AlF_4^- and AlF_6^{3-} at different temperature, one can find that with the increase of temperature, the peak of AlF_6^{3-} becomes stronger relative to that of AlF_4^- . That indicates that the amount of AlF_6^{3-} increases with temperature.

As also can be seen from the data in Table I, with the increase of the molar ratio between NaF and AlF_3 , the relative intensity of the peak at ~555 cm^{-1} increases and that of the peak at ~624 cm^{-1} decreases. That means that there are more AlF_6^{3-} and less AlF_4^- in the melts with higher molar ratio between NaF and AlF_3 .

However, the change law of the parameters of the peak at ~500 cm^{-1} is not obvious. It only can conclude that the relative amount of the corresponding ion complex increases with the temperature.

Conclusions

In this paper, the ionic structure in NaF-AlF₃-NaCl melts with different molar ratio between NaF and AlF_3 and NaCl contents at different temperature are studied by UV Raman spectroscopy with a closed sample cell. The change law with temperature and composition are analyzed. The following conclusions are obtained.

- (1) The main ion complex in the research melts are AlF_4^- and AlF_6^{3-} , and the resultant of the substitution of F^- in Al-F complex by Cl^- may exist in the melts.
- (2) With the temperature increasing, the structure of the complex becomes looser and more unstable, and the amount of AlF_6^{3-} increases.
- (3) With the increase of the molar ratio between NaF and AlF_3 , the amount of AlF_6^{3-} increases and that of AlF_4^- decreases.

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