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STRUCTURAL DIAGNOSTIC OF HIGH TEMPERATURE LIQUID PHASES BY ^{27}Al NMRD. MASSIOT^{**}, F. TAULELLE^{*} and J.P. COUTURES

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Résumé - L'amélioration des procédés de soudage par plasma ou laser suppose une bonne connaissance des propriétés microscopiques du liquide constituant la zone fondue. Le développement de nouvelles sondes de résonance magnétique nucléaire permet d'atteindre cet objectif. L'analyse de la raie de résonance de ^{27}Al dans des oxydes liquides alumineux montre un régime d'échange rapide entre des coordinences quatre, cinq et six et une dépendance de la position de cette raie en fonction de la composition du liquide.

Abstract Improvements of welding processes by plasma or laser require a good knowledge of the microscopic properties of the liquid associated to the melted area. The development of new high temperature NMR probes allows to reach such a goal. In the case of alumina bearing liquids, the analysis of the ^{27}Al resonance line shows a rapid exchange regime of Al in four, five or six fold coordination together with a dependence of the resonance line versus the liquid composition.

1 - INTRODUCTION

NMR is a well suited spectroscopy for the study of the liquid state and is widely used by organic chemists (^1H and ^{13}C with or without cross polarization). Its development, in the high temperature area for non metallic materials, has been slowed down by technological problems : high magnetic fields ($4 < H_0 < 11 \text{ T}$), interactions between the material under investigation with its holder imperatively a dielectric, time life of the radio-frequency components at temperature higher than 250°C .

The first significant results have been obtained recently /1 - 3/ on liquid silicates up to 1300°C or at higher temperature (2100°C) on aluminum bearing oxides /4/. Even if the signal intensity decreases with the temperature according to a Curie Law, the motional narrowing improves largely the dynamic of the signal. So if the sample under study and the RF components of the probe are thermally

decoupled ($S/N = f(1/T)$) it's easy to get a high signal to noise ratio and so representative data within a reasonable period of time.

We present here a new type of radio-frequency resonator with improved performances and obtained results on high temperature alumina bearing liquids.

2 - EXPERIMENTAL

The probe head, jointly patented with Bruker [5] operates in axial configuration and is schematically shown Figure 1. Such a type of probe could be multinuclear or mononuclear and in this case optimized for a given nuclei (^{27}Al , ^{17}O ...). In all cases the sample is aerodynamically levitated by a flowing gas (Argon, air, oxygen) at 1.5 lmn^{-1} . The convergent - divergent nozzle of the levitator structure is also the resonator of the radio-frequency circuitry for the mononuclear probe or is inserted in a modified VSP Bruker multinuclear probe. In this case, the levitator is made with BN. For the both probes the sample part and the RF circuitry are thermally decoupled. The typical experimental conditions are RF resonance frequency 78.21 MHz for ^{27}Al ($H_0 = 7\text{T}$), spectral width 125 kHz, excitation time $40\mu\text{s}$ with a dead time of 0.5 s between each pulse, acquired points 4.096, accumulated scans 130.

The heating of the sample is provided by a CW CO₂ laser (MPB Technologies - Canada) with a power continuously variable between 20 and 120 W.

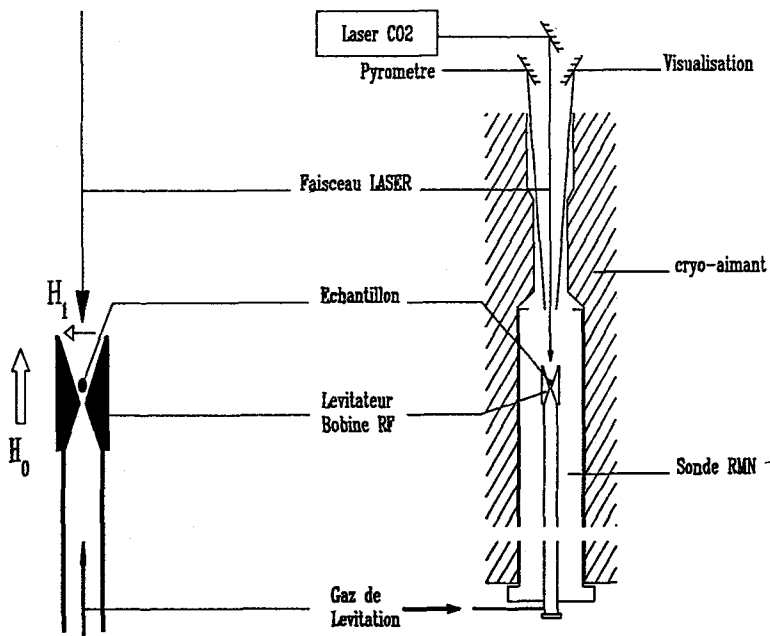


Fig.1 Set up of the aerodynamic high temperature probe

3 - RESULTS AND DISCUSSION

As a first example Figure 2 shows the spectrum obtained when the CO₂ laser beam (P = 60 W) interacts with a porous silica - alumina ceramic (mainly mullite) giving a partial melting. In this case the target is a cylinder of 10 mm diameter, 5 mm high and the melted volume around 3 mm³.

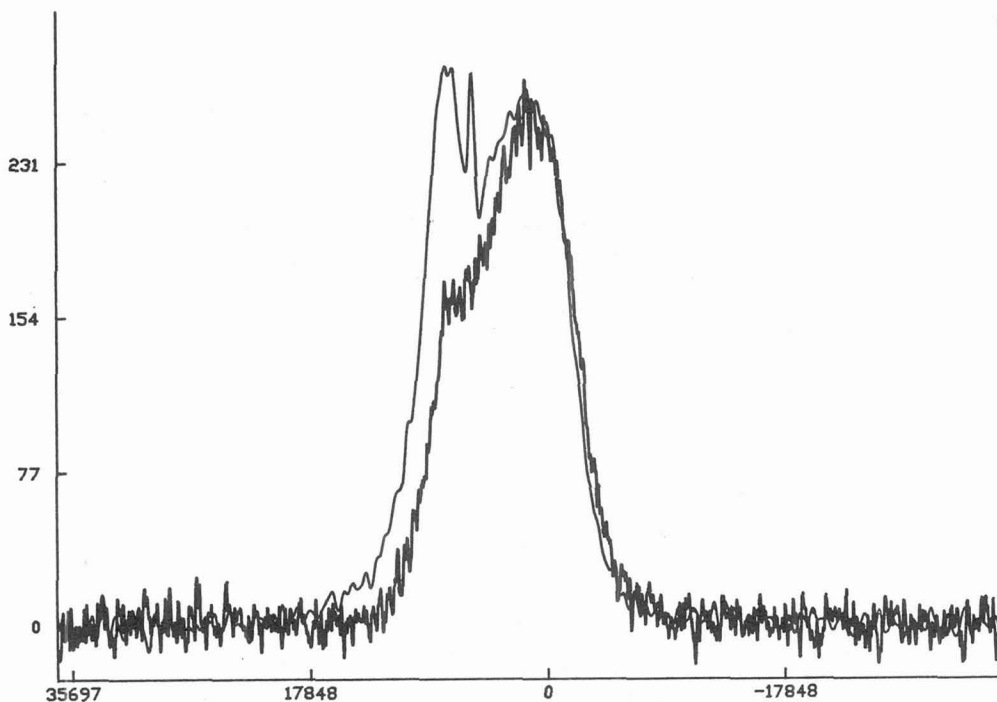


Fig. 2 : ²⁷Al resonance line of a silico-alumina ceramic

The darkness resonance line is obtained at room temperature under static conditions. This broad band (- 1/2 - 1/2 transition) is due to the strong quadrupolar coupling of ²⁷Al (S = 5/2) and also to the irradiation conditions. When the temperature increases (i.e the CO₂ laser power) a partial melting occurs and a very fine peak is then observed. Its intensity grows up to the obtention of a thermal equilibrium regime (i.e melted volume) under the experimental conditions. The broad band is still present with a modified shape with a most finer component that we relate to the increase of the Al motional narrowing in the solid part with the temperature.

Figure 3 shows the ²⁷Al resonance line of pure Al₂O₃ and Y₃Al₅O₁₂ liquids under air at a temperature slightly higher than their corresponding melting points. The resonance line exhibit a sharp profile of pure Lorentzian type. This fine line indicates, like in Figure 2, a fast exchange regime between the different possible coordination of Al in these liquids. The time scale (~ 10⁻⁹s) is too long to resolve the contribution and so the population of the different sites.

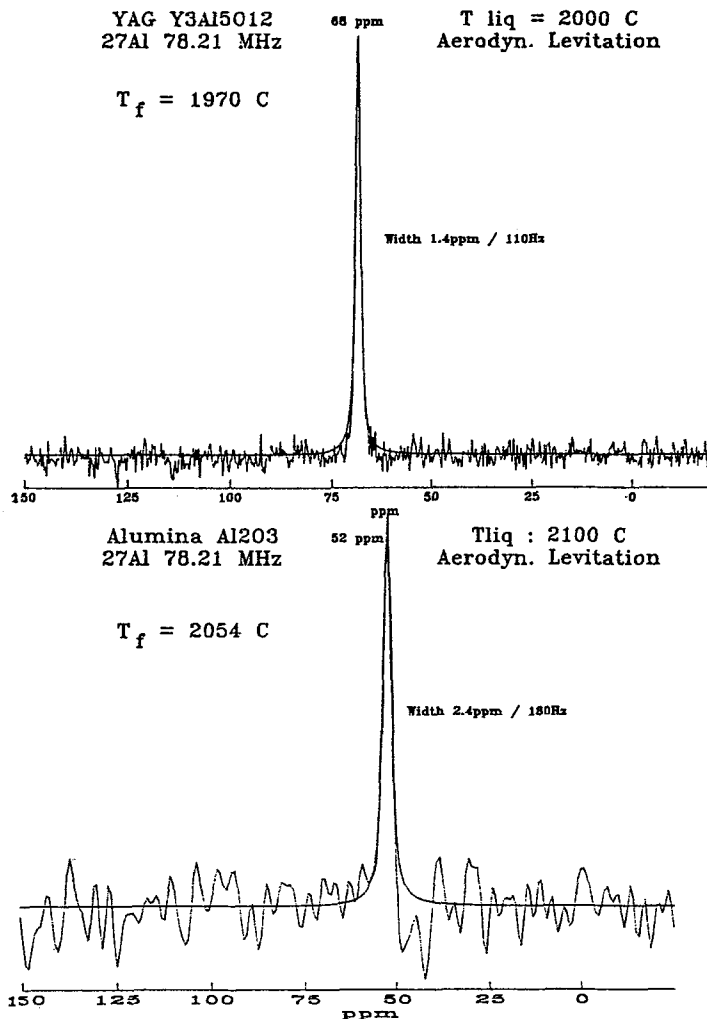


Fig. 3 : ^{27}Al resonance line of a liquid Al_2O_3 and $\text{Y}_3\text{Al}_5\text{O}_{12}$

The observed chemical shifts δ (reference ^{27}Al resonance line of $\text{Al}(\text{H}_2\text{O})_6^{3+}$ in nitric aqueous solution at room temperature expressed in ppm) are reported Table 1. The position of the maximum of the resonance line is mainly related to the coordination of Al and the averaged Al-O distances of the coordination polyhedra. We observe for Al in non silicated melts a range of δ varying from 52 ppm (Al_2O_3) up to 82 ppm ($0.37 \text{ Al}_2\text{O}_3 - 0.63 \text{ CaO}$ liquid). The range of chemical shift is more larger than for the solids (10 ppm for fourfold coordinated - 75 ± 5 ppm ; 10 ppm for Al in octahedral coordination 5 ± 5 ppm). Some of the results obtained are given Table 1 where for each compound the data on the corresponding solid are shown. These data have been obtained on crystallized samples by the Bruker MAS (Magic Angle Spinning) probe operated at a frequency of rotation of 15 kHz.

4 - FUTURE AND CONCLUSION

We have reported here new experimental results obtained during the last four months and focused only on Al atoms. These experiments are in progress and the final set up which is planned to be in working conditions end of 1990 is shown Figure 4. This set up must allow to operate with a better temperature homogeneity by the use of two lasers to heat simultaneously the upper and the lower area of the target. In this case the NMR spectrometry itself could be used to carry out temperature measurements without the necessity of the knowledge of the emissivity.

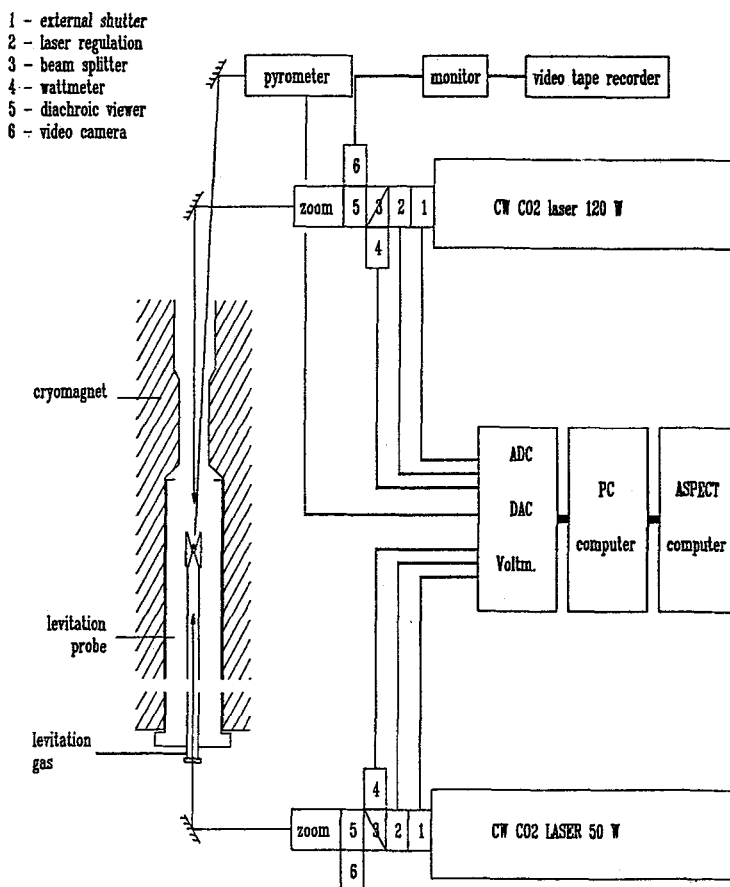


Fig.4 set up of the improved high temperature NMR spectrometer

A specific, optimized ^{17}O probe is planned to be in operation at the same time and so information on oxygen could be available. Even if ^{17}O has a very low natural abundance (0.036%), very interesting results have been obtained on low viscosity liquids (K_2SO_4 - Na NO_3 mixtures) indicating that liquids having an atomic concentration of ^{17}O in the percent range could be studied. Very recently ^{17}O MAS-NMR results on solid oxides have been obtained without any enrichment /7/. As stated previously we have focused this paper only on the study of liquid which are isotropic medium

TABLE I : ^{27}Al NMR results on alumina bearing material

COMPOUND	Tf (°C) IPTS 68	Solid			Liquid
		group struct.	% Al IV % Al VI	δ Al IV δ Al VI (in ppm)	δAl obs (in ppm)
CaAl_2O_4	1605	Orth. $P2_1/n$	100	75	70
LaAlO_3	2110	Rh R3C	0	--	74
Y AlO_3	1970	Orth.	100	9	71
$\text{Y}_3\text{Al}_5\text{O}_{12}$	1970	C Ia3d	0	--	71
$\alpha\text{Al}_2\text{O}_3$	2054	Rh R3C	100	7	68
			60	76	
			40	0	
			0		53
			100	9	

For liquid Al_2O_3 and yttrium aluminium garnet (YAG) the full width at half maximum of the resonance line is respectively 2.4 and 1.4 ppm. Such a parameter is related to the statistic disorder of configuration of the site under examination plus in the case of high temperature experiments a contribution to the temperature gradient in the sample. The effect of the atmosphere (oxygen potential of the flowing gas) is under examination and shows a complex behavior. Even if the thermal conductivity of argon and oxygen are quite different leading to a possible variation of the sample temperature an effect of the oxygen potential of the flowing gas on the melt is observed. This is particularly clear with liquid YAG and is coherent with previous results on the observation by EPR of paramagnetic defects of Al-O-O° type on glassy YAG only when the corresponding liquid is melted under air or oxygen /6/. The FWHM could also be dependent of the oxygen partial pressure of the levitation gas (Al_2O_3 Argon 100 Hz oxygen 72 Hz ; YAlO_3 Argon 70 Hz - oxygen 124 Hz).

The sensivity of this approach to the liquid composition was checked on commercially available electrically melted ceramics (SEPR, Jargal Trade Mark). The results are reported Table 2. In a first analysis we could say that the population of octahedral Al^{3+} in these liquids decreases versus their Al_2O_3 molar content.

TABLE 2 : Chemical of ^{27}Al in Jargal family liquids

Jargal Name	Composition (mole %)				δAl obs ppm
	Al_2O_3	SiO_2	Na_2O	MgO	
M	95.6	0.54	3.8		56.4
H	93.7	0.14	6.1		62.8
N X 5312	86.9	0.36	4.7	8	64.7

nevertheless the use of selective and non selective pulse sequences allows to study biphasic mixtures (liq + sol). Direct information on the motional narrowing of the nucleus under investigation could also be obtained by T_1 measurements. Special probes working under a known VT allows also to carry out measurements on autodiffusion coefficients.

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