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High temperature X-ray diffraction investigation of an aluminium-silicon-corundum system

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Abstract. All aluminium products come from melting processes. At the melting temperature, aluminium and its alloys are highly reactive with the metals and the refractories which line the furnace inside. Investigation of interactions of aluminium and its alloys with the refractory materials upon heating is therefore an issue. In this paper this investigation is focused on the model system made of aluminium-silicon mixture at eutectic composition and corundum. In particular, the structural and microstructural features are investigated by high-temperature resolved X-ray diffraction (HTXRD) and bidimensional micro X-Ray diffraction (XRD^2). During cooling we followed the crystallization of aluminium and silicon and few single crystallites of a new phase, possibly related to $Al_{19}Fe_5Si_2$, were detected by microXRD^2.

Introduction

The economic importance of the aluminium industry is based not only on the production of aluminium itself but also on the appeal that it emanates from a wide range of fields upstream and downstream of aluminium production. It is a growth sector that contributes to promote technical progress and improve living standards (mobility, safety, healthy eating) as a result of close co-operation with nearly every branch of industry.
Aluminium manufacturing requires melting and molten aluminium can be a very aggressive metal with respect to other metals and ceramics. This property causes serious problems, as it may etch the materials employed for containment of molten aluminium together with the refractories exposed to bath vapours. Thus, aluminium industry put large effort in choosing furnace lining materials that minimize or eventually eliminated this phenomena.
Among these phenomena we focus on the process which consist of penetration by the melt of lining material and subsequence formation of metal-ceramic interphase layers [1]. This inter-

phase nucleates at the molten aluminium/vapour/refractory interface. The nucleation/growth of the interphase is driven by the continuous solidification and melting occurring at this interface. The solidification/melting cycles is provided by temperature variation due to the level fluctuations of the aluminium bath. Indeed, the literature is poor of structural studies about this metal-ceramic interphase. Some works have been carried out by Wynn [2], Afshar et al. [3], Shen et al. [4].
In this study we consider aluminium-silicon-corundum system where aluminium and silicon play the role of the melted alloy bath, and corundum plays the role of the refractory. In particular, we tracked the structural evolution of this system upon a heating/cooling cycle by high-temperature resolved X-ray diffraction (HTXRD). HTXRD information were integrated by bidimensional micro X-Ray diffraction (XRD^2) [5] and by differential scanning calorimetry (DSC). HTXRD experiments were conducted in conditions as close as possible to real conditions (i.e. into the furnace). However, in order to make the experiment reproducible and feasible, we adopted vacuum conditions.
Indeed, at the best of our knowledge, this is the first study which employs HTXRD and microXRD^2 to investigate these systems.

Experimental

Sample was prepared by mixing powders of corundum and aluminium-silicon mixture at eutectic composition (Pometon S.p.A, Italy) in weight proportion corundum/mixture equal to 4.8 w/w. The powders (172 mg) were then pressed in a cylindrical tablet 13 mm large and 0.7 mm thick. The tablet thickness was set to 0.7 mm as this value gives a satisfactory compromise between tablet mechanical resistance and X-ray linear absorption in order to make the HTXRD experiments to be feasible with the experimental setup described in the following.

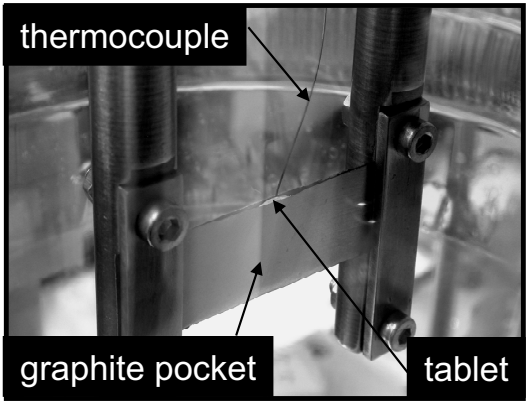

Figure 1. Experimental chamber

HTHRD measurements were performed on a custom horizontal $\theta/2\theta$ Bragg-Brentano diffractometer equipped with a high temperature chamber working in vacuum conditions [6]. The tablet was held by a graphite pocket which also served as heating element. Temperature control and feedback were achieved by a thermocouple put in contact with the sample and the graphite pocket. The chamber setup is showed in figure 1; more details can be found in Ref. [6]. Mo $K\alpha$ radiation (λ = 0.7093 Å), generated by a sealed X-Ray tube with a rotating anode (Rigaku), and a proportional counter (Philips) were used for the experiment. The temperature cycle of the experiment consisted in (1) heating from ambient temperature up to 620 °C at a heating

rate of 1.5 °Cmin^{-1} and (2) leaved to freely cool back to ambient temperature. During the cycle the sample was scanned every 30 °C. All the scans were collected in isothermal condition and 5 minutes after the target temperature was reached (in order to allow for temperature equilibration). The angular range of all the scans was 7.00 deg < 2θ < 39.00 deg, with step size and time of 0.04 deg and 5 s, respectively.

MicroXRD^2 experiments were performed using a D-Max Rapid system equipped with Cu Kα (λ = 1.5406 Å) sealed X-Ray tube and a bidimensional image plate detector (Rigaku). All the microXRD^2 patterns were collected by illuminating the sample with a beam collimator of 300 μm diameter.

DTA measurements were performed by a SDT Q600 (TA Instruments), at a heating rate of 10°C min^{-1}, under Ar atmosphere, and with Al_2O_3 pans as sample holder and reference.

Results and discussion

Figure 2(a) shows the HTXRD diffraction patterns of the sample collected in isotherm from 27°C up to 620°C. By comparison with the reference patterns reported in figure2(b) it appears that the pattern of the sample collected at 27°C is the sum of the Bragg's peaks belonging to cubic aluminium [7], cubic silicon [8] and rhombohedral corundum [9] phases.

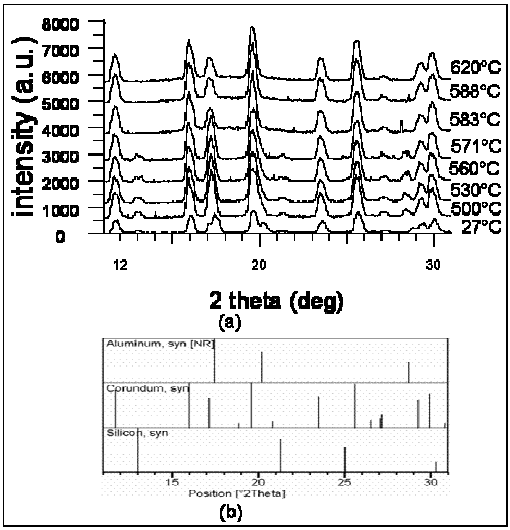

Figure 2. (a) HTXRD patterns collected during heating; (b) Reference peak positions and corresponding peak indexing for corundum [7], Al [8] and Si [9].

These are the phases of the original materials mixed for preparing the sample tablet. Such phases remain in all the patterns collected from 27°C to 571°C, while in the pattern collected at 583°C and in the subsequent patterns up to 620°C they disappear and only the corundum phase remains. This tracks aluminium and silicon melting.

It follows that under heating the patterns reflect the phase transformation we expected, as the aluminium and silicon phases belong to the eutectic alloy, whose nominal melting temperature is about 577°C [10], while corundum melts at a temperature higher than 2030 °C. However, we checked the melting point of the employed Al-Si mixture at eutectic composition by DTA, which confirmed the value (we measured a melting point of 577.54°C).The formation of a new phase with respect to the raw

mixture occurs during cooling, yet at a temperature close to the melting point, as can be seen in figure 3.

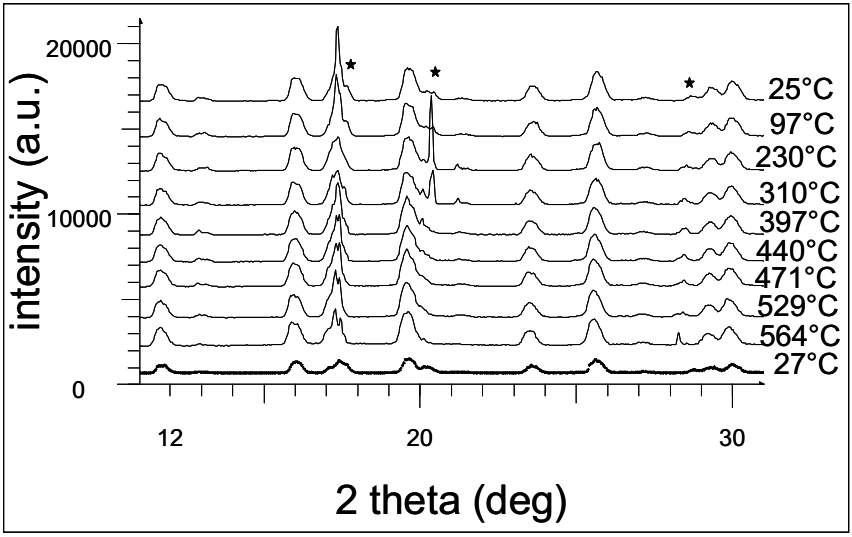

Figure 3. HTXRD patterns collected during cooling (standard line patterns); the bold line pattern is the one collected at room temperature before the heating/cooling cycle and it is reported here to ease the comparison

This figure shows the patterns collected during cooling from 564 °C down to room temperature (25 °C), and, in order to ease the comparison, it also shows the pattern of the sample collected at room temperature at the beginning of the heating/cooling cycle (this pattern is in bold line). At 564°C we observe the recrystallization of cubic Al and cubic Si. Furthermore, in this pattern some other peaks (highlighted by the stars), that cannot be attributed to cubic Al, cubic Si or corundum, can be detected.

These peaks become clearer and sharper as the cooling process advances. The pattern collected at the end of cooling therefore evidences the cubic Al, cubic Si and rhombohedral corundum phases plus a new phase (or new phases).

Additional information on the sample microstructure and further insight into the new phase were gained by microXRD^2 experiments. The salient results are shown in figure 4. Figures 4(a) and 4(b) report the XRD^2 patterns of the sample before and after the thermal cycle, respectively.

The Debye's rings that appear in the patterns show remarkable differences. Corundum Debye's rings, indicated in the figure by C, are identical before and after thermal cycle. With "identical" we mean that they have the same 2θ positions, and that they are identically continuous and sharp. It follows that no structural (in agreement with HTXRD) nor microstructural change in the corundum phase happened during the cycle [5]. This confirms that corundum (which in the experiments was intended to play the role of the refractory) does not interact with the Al-Si mixture.

Instead, comparison between the Al Debye's rings (indicated in figure 4 by A) before and after the cycle suggests both structural and microstructural changes. Actually after the cycle the Debye's rings become spotty. In particular, spotty Debye's rings imply that the Al phase did recrystallize in bigger crystallites. This is probably a consequence of phase separation in the molten Al-Si mixture. Analogous considerations can be drawn with regard to the Si phase, as also its Debye's rings (indicated in figure 4 by S) become spotty upon the cyclic heat treatment.

In figure 4(b) Bragg's spots belonging to other phases than Al, Si and corundum appear, as it can be better appreciated in Fig. 4(c), which is the magnification of the white squared areas of figure 4(b). These spots allowed the indexing of the new phase, as they made possible to identify and resolve a greater number of Bragg's reflections with respect to what could be got from the HTXRD patterns. Namely, these spots, corresponding to interplanar distances of 2.3 Å, 2.0 Å, 1.41 Å and 1.21 Å, that can be indexed by a cubic cell with the cell parameter a=4.0 Å.

This result recalls the observations contained in a recent paper by Kral et al. [11]. In this work, which covers phase transformations of Al-Si eutectic alloys, the formation of a cubic intermetallic phase $Al_{19}Fe_5Si_2$ is assessed.

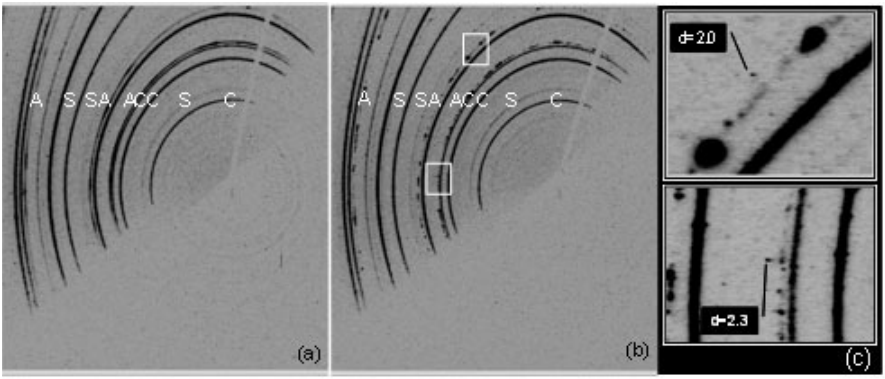

Figure 4. microXRD[2] images of the sample (a) before thermal cycle and (b) after the thermal cycle; (c) magnifications of the white squared areas.

Existence of Fe in traces in the aluminium-silicon alloy and its effect on (re)crystallization are known. Actually, iron is a natural impurity in even "high-purity" aluminium. It is also known that it plays a significant role in the formation of Al-Si eutectic alloy (in the literature Fe is also referred as eutectic modifier). Indeed iron resulted in the formation of iron containing β-(Al, Si, Fe) phase that plays an important role in the nucleation of the eutectic phases [12].

The presence of Fe impurity, in our sample, was checked by X ray fluorescence experiments (less than 1% wt.) and may also give an explanation to the structural and microstructural changes we found in the Al and Si phases upon the thermal cycle. The impurity may drive, together with the nucleation of the Al-Si-Fe phase, different crystallization (kinetics) of the

Al and Si phases. In the present case the effect results in bigger crystallites. This work shows that iron, even in traces, may play a relevant role in the crystallization of Al/Si system.

Conclusions

In this paper, chemical etching between melted aluminium alloy and refractory has been studied by means of high-temperature X-ray diffraction for the first time. A system composed by aluminium-silicon mixture at eutectic composition and corundum, where corundum plays the role of the refractory, was chosen as model system. The system was studied during the heating/cooling cycle and its structural and microstructural evolution tracked by HTXRD and microXRD^2.

Under heating the system behaves as expected (melting of the aluminium-silicon eutectic alloy at 577°C). During cooling we observe the recrystallization of cubic Al and cubic Si and a new phase was detected. Both the aluminium and the silicon phases are made up of bigger crystallites than in the raw materials. The new phase was indexed by a cubic cell with a cell parameter of 4.0 Å. On the basis of the literature results [11,12] and the presence of iron impurities detected by XRF, we believe that the new phases is an Al-Si-Fe phase.

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