

# THE 4TH INTERNATIONAL CONFERENCE ON ALUMINUM ALLOYS

## CARBONACEOUS INCLUSIONS IN ALUMINUM ALLOYS

Omar Quintero-Sayago and Sonia Ramírez C.

Universidad Simón Bolívar. Departamento Ciencia de Materiales. Apartado 89.000. Caracas.  
Venezuela.

### ABSTRACT.

Chemical distribution, taken inside two carbon containing inclusions of idiomorphic and dendritic morphologies, is used as a proof to discuss their probable formation mechanism in aluminum melt. The nucleation potential of the Al-Si-C particles in the liquid is explained, based on the interactions between Si and C, partially depending on the hypothesis of qualitative semi-empirical concepts of alloy theory when applied to the liquid state. Even though the tendency for Al-Si bonding in liquid is more favorable to exist, high surfactancy on halide salts promote wetting. This enhance the generation of carbonaceous inclusions in the melt.

### 1.- INTRODUCTION.

The study of liquid metals, their properties and the relation between the latter and the solidified metal has considerable importance due to both the chemical reactions taking place in the liquid and the influence of their products on the properties of the metal. Particularly the size, the shape, the type and the distribution of inclusions present in the products are the performance fingerprints of the cast shop<sup>[1]</sup>. We refer here as inclusion to any solid or liquid phase present above the liquidus temperature of a particular alloy. From the point of view of its origin, inclusions found in alloys are commonly classified as primary and secondary<sup>[2]</sup>. In aluminum, nonmetallic and intermetallic inclusions are generally classified by type and origin as: exogenous and insitu<sup>[3]</sup>. Those non metallic particles that are imported to the molten metal stream from external sources are referred to as exogenous. Their sources include occluded particles on and within primary and secondary ingot. Inclusions formed as a result of chemical reactions within the melting metal handling system are known as insitu. This source of inclusions is prevalent and often insidious, due to the strong

thermodynamic driving force for reaction<sup>[3]</sup>. When inclusions are liquid, they are usually deformable and they may coalesce.

Solubility is thermodynamically analyzed from the heat formation of mixtures of the involved components. In metallurgy, cohesion of alloys means the difference in enthalpy between the alloy and the elements, which is usually called heat of formation<sup>[4]</sup>. Strictly speaking cohesion is free energy, but for most metals the term enthalpy will be enough. Heat of formation or solution improves the distinction between more soluble and less soluble elements. Then the heat of mixing of liquid alloys is derived from the change in boundary conditions in those positions where there are contacts between dissimilar atoms<sup>[5]</sup>. One effect is charge transfer, that will influence the atomic volume. The state of dissolved elements can be broadly ascribed to the increase in cohesive energy due to donation of an electron from solutes to empty bonding p- or d-orbitals in the solvent.

As electrons are the universal glue for all materials, the solution of elements in molten metals is due to breakdown of the bonds in the liquid and the formation of new ones between atoms of the metal and the added elements<sup>[6]</sup>. The chemical bonding description of the interactions of electrons with one another and with the nuclei of atoms is a general model that is equally applicable to metallic and nonmetallic materials. The nature of the bonds is in turn, governed by the electron structure of these substances<sup>[6]</sup>. In the valence bond-model, the cohesion of atoms is ascribed to overlapping of atomic orbitals to allow the electrons to occupy bonding orbitals in which they can interact with two or more nuclei and hold them together<sup>[7]</sup>. For effective bonding, it is necessary to promote to various excited electronic configurations to be able to make effective use of the valence electrons in bonding<sup>[7]</sup>. Promotion means the energy to promote one electron out of the valence s and into the valence p- or d-shell in the neutral atom<sup>[5]</sup>.

Table I. Electronic properties of elements under consideration.

Element	Outer Electronic Configuration		Interatomic Bond Energy Kcal/g-at	Ref.
	Ground State	Promoted		
Al	3s <sup>2</sup> 3p <sup>1</sup>	3s <sup>1</sup> 3p <sup>2</sup> [8]	77.5	[9]
C	2s <sup>2</sup> 2p <sup>3</sup>	2s <sup>1</sup> 2p <sup>3</sup> [8]	170	[6]
Si	3s <sup>2</sup> 3p <sup>2</sup>	3s <sup>1</sup> 3p <sup>3</sup> [8]	108	[6,9]
B	2s <sup>2</sup> 2p <sup>1</sup>	2s <sup>1</sup> 2p <sup>2</sup> [9]	135	[9]

Table I shows the most important electronic characteristics of some of the selected types of atoms considered in present study. If it is physicochemically assumed that some of the atoms of a melt are in the form of ordered groupings in regions of the order of tens of angstroms, called clusters; the other group of atoms of the liquid are moving in complete disorder<sup>[6,10]</sup>. It means that inside a

liquid alloy, there are motions characteristic of solid as oscillations about a position of equilibrium and also of a gas such as random migration; in consequence, any particle can pass from one group to the other. Of course, clusters of ordered atoms in liquid have limited solubility of solute elements<sup>[6]</sup>; then the remainder of solutes must be situated in an environment of disordered solvent atoms. The limiting link in the process of solution of solutes in molten aluminum is the number of the disordered solvent atoms with the capacity for accepting valence electrons from solutes<sup>[6]</sup>.

## 2.- EXPERIMENTAL.

A 6 mm thick strip (Al + 0,25%Si + 0,50%Si + 0,01%Mn), was manufactured by twin-roll continuous casting process. In order to be observed under the optical and the scanning electron microscopes, the specimens transverse surface was carefully hand polished and ultrasound cleaned using ethanol. SEM observations were conducted in unetched condition; both Point and X-ray Line Profile Analysis were taken from the observed particles. The X-ray Line Profiles were recorded after an average of 10 scans in 55 periods per scanned line. The window full scale for elements were, respectively, 250 for boron and carbon, and 2500 for aluminum and silicon.

## 3.- RESULTS.

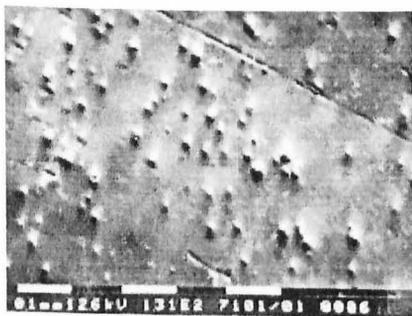


Fig. 1. Polished microstructure as seen at low magnifications.



Fig. 2. Photomicrograph where X-ray line profile was performed.

The SEM photomicrograph of figure 1 at 130 x, reveals the transverse polished surface. Figure 2 is the SEM magnified view of one of the idiomorphic particles. Its X-ray line profile of elements Al, Si, and C are disclosed in figure 3. The left side of the SEM photomicrograph of figure 4 at 2500 x is an evidence of the dendritic morphologies; the right handside area shows the other type of particle. Point analysis shows their Al and Si concentrations are 32.79 and 67.33 atomic percent, respectively. Figure 5 at 2500 x amplifies the dendrite-type particles seen in the left side of figure 4;

its correspondent X-ray line profiles for elements B and C are exhibited in figure 6. The point analysis of dendrite-type particles, evidence they also contain elements Na, Al, Cl, and K in concentrations of 2.828, 91.519, 3.902, and 1.750 weight percent, respectively.

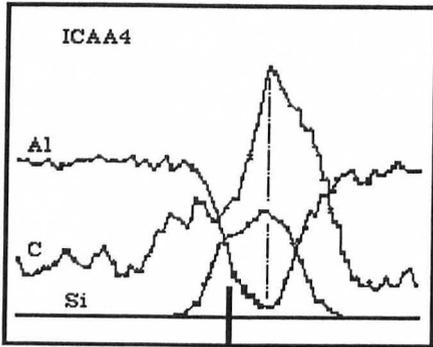


Fig. 3. X-ray line profile shown on photomicrograph of figure 2.



Fig. 4. Detail of the carbonaceous particles present in figure 1.



Fig. 5. Dendritic type morphology.

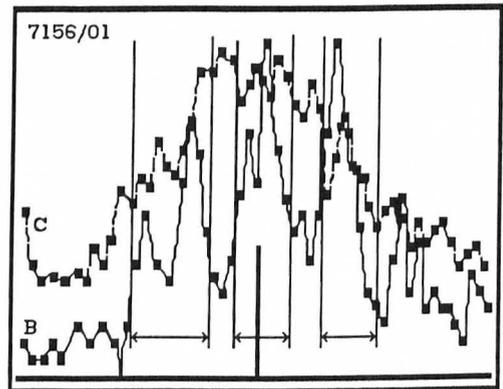


Fig. 6. X-ray line profile of figure 5.

#### 4.- DISCUSSION.

The photomicrographs of figures 2 and 4, exhibit the idiomorphic morphology of the particles shown in figure 1. They all contain Al-Si-C as evidenced in their X-ray Profiles (figure 3). When these type of particles were observed under the optical microscope at 400 x or higher magnifications, their reflectivity looked similar to particles from the grain refiner. However, the EDS analysis showed completely different chemistry. A careful observation of the X-ray line

profiles, figure 2, indicates that inside the idiomorphic particles both carbon and silicon show similar distributions, and that aluminum behaves in an opposite way. Figure 3 displays a continuous depletion of aluminum from the outer side of the particle towards its center. Carbon and silicon continuously increase their concentrations, revealing a maximum in the center of the precipitated particle. Inside the interparticle areas, carbon distribution presents a different behavior in relation to silicon. The latter is depleted while carbon distribution is slightly lowered, indicating very small carbon rejection during solidification, which allows to think that inside these two regions, carbon is equally distributed. These conduct suggest they were originated during melting due to some type of liquid reactions among the three elements and some others like<sup>[11,12]</sup> Cu, Mn, and Cr, when present.

To analyze the liquid alloy, carbon sources are important to be considered due to hydrocarbon surface contaminants, such as those found on painted scrap, oil, grease, and residual lubricants which pyrolyze at melt temperatures to produce Al-Si-C liquid particles as suspended insitu inclusions<sup>[3]</sup>. The insitu formation of aluminum carbide involves energetically aided reactions between aluminum, elemental carbon, or carbon containing compounds, for these reactions to occur, carbon containing reactants require wetting characteristics for carbon, which means intimate interphase contact between aluminum and the carbon source. Virtually, all volatile hydrocarbons are viable sources of carbon promoting reaction with aluminum. This is particularly possible when both molten salts and high temperatures are present<sup>[3]</sup>.

On trying to develop a physical understanding of the interatomic forces which compel silicon and carbon to interact in liquid aluminum, let us consider some semi-empirical aspects of the bonding concepts of liquid alloy phase formation. The semi-empirical alloy theories are based on the thermodynamic theory of regular solutions<sup>[4]</sup>, then it is necessary to focus on those interactions in the alloy which are symmetric between A-B atoms pairs in the clusters. In hypoeutectic liquid aluminum alloys, is postulated that silicon forms compounds of Al-Si clusters<sup>[13]</sup>. As consequence, inside the melt their distribution behaves like if aluminum-silicon clusters have higher densities than the liquid<sup>[13]</sup>, then they have the tendency to settle and are randomly distributed inside the liquid alloy. A probable explanation to the C-Si-Al interaction phenomena may be found in the different solubilities of these elements in both phases and also in the competition between the metal and non-metal atomic binding forces. The greater the imperfection of the electron valence band of the solvent, the higher is its acceptor capability and more solute dissolves<sup>[14]</sup>. By virtue of s  $\rightarrow$  p electron transfer, some of the conductivity electrons inevitably go over into p-band, lowering the number of uncompensated p-electrons and correspondingly lowering the interatomic interaction energy<sup>[14]</sup>. The incomplete p-orbitals lead to an exchange equilibrium between s-p valence electrons.

Silicon and carbon are s-p elements since they have only unpaired s and/or p electrons. In their ground state their outer electronic configuration are not well suited for bonding because the  $2s^2$  pair is a completed sub-group. Then for reactions it is necessary to consider the structure of the hybrid  $sp^3$  bonding orbitals<sup>[8]</sup>. To form a solution in liquid aluminum, those elements have to interchange some electrons of their outer electronic configuration<sup>[15]</sup>. In liquid aluminum, Si is competitor to C as valency electron donor<sup>[16]</sup>. What it means is that they inject valency electrons into the s-band of Al to increase the concentration of mobile C-electrons in the liquid. These electrons are responsible for the bonding in the clusters and consequently, their number and size increase, enhancing the submicroheterogeneity of the liquid<sup>[6,16]</sup>.

In aluminum dilute alloys, the C and Si atoms are supposed to be arranged in the free volumes of the molten metal around the disordered Al atoms. Accordingly, the regularities revealed on figure 3 for C and Si profiles could be interpreted from the standpoint of the donor-acceptor electron properties of these elements with respect to aluminum.

In each group of the Periodic Table, the stability of the excited  $s^{(1)}2p^x$ -configurations of valence electrons decrease, as the main quantum number increases. Also, their interatomic bond energies are governed by their  $sp^3$ -configurations<sup>[6]</sup>, due to competition between the Al-Si and the Al-C reactions. Then, some space around the substituent Si atom in the aluminum quasi-lattice of Al-Si-C melt is a forbidden zone for the Si atoms<sup>[6,14]</sup>. What it means is that the resulting Si-C forces of repulsion, narrow the regions of statistically uniform distribution and of the free displacement of the Si atoms<sup>[6,14,16]</sup>.

Other important factor to be considered is that Si rise its covalent bonding breakdown with the increasing temperature<sup>[6]</sup>, this means an increase in its reactivity inside the liquid. Then both, the lowering in strength of the electronic excited configuration and the increase in reactivity of Si justify the tendency of Si to bond with Al atoms rather than to form Al-C bonding in the melt. In other words, Al-Si bonding pairs are more favorable than Al-C clustering, as seen from Table I. At melting temperature, there also exist C-C and Si-Si clusters floating in the melt where all of them survive as viscous particles.

The previous discussion explained why silicon distribution at interparticle location is depleted in comparison to carbon distribution in the same spaces. Since liquid inclusions are deformable phases, its entrapment by filtering systems is very difficult, although the clusters had coalesced. This poses complexities not confronted with solid inclusions<sup>[3]</sup>. Accordingly, they could survive

within the melt, since their response to the surrounding fluid forces is far different to solid particles<sup>[3]</sup>.

The maltese-cross morphology seen in figure 4 the EDAX technique unambiguously identify Al-Na-Cl and K also show they incorporate C and B. X-ray line profiles of the latter are seen in figure 6 where inside the dendrites it is possible to see that carbon and boron have alike distributions. In the interdendritic regions they have an opposite behavior, now boron distribution is depleted. The existence of sodium and potassium inside the dendrites suggest that this type of particle has originated from solid halide salts present in the liquid as a second immiscible liquid phase, due to fluxing additions during the melting process. The reason is that when solid halide salts are present in liquid aluminum, due to the presence of surface active elements, they are surrounded by aluminum carbides<sup>[3]</sup>. So these elements are responsible to promote wetting, which is directly related to the contribution to contact and ion exchange with carbon sources<sup>[3]</sup>. In consequence, the Al-C reactions become operative by enhancing the generation of carbonaceous particles into the melt.

In this case, surfactancy strongly compete with silicon-aluminum electron interactions, causing silicon absence inside the carbon floating viscous particles. The promoted electronic configuration of B is substantially more stable, when compared to the excited state of aluminum, seen in Table I. Then, after grain refining addition, partial content of B is dissolved into the flowing aluminum, to enhance the promoted  $2s^1p^2$  boron incorporation into the deformable viscous carbonaceous inclusions. After solidification, they may appear in the microstructure in a variety of sizes and morphologies<sup>[3]</sup>, depending on interface kinetics, relative surface energies, collisions, and inclusion viscosity<sup>[2]</sup>. Of course, at rapid cooling rates, as in twin-roll continuous casting process, the insitu inclusions can have a dendritic or cellular morphology when their growth is limited by diffusion from the melt<sup>[3]</sup>. Probably carbon supersaturation is the cause for this limiting effect as evidenced by boron depletion inside interdendritic morphology regions in figure 6. This corroborates why carbon is just present into the inclusions. However, boron depletion is a consequence of solute interactions in front of the liquid-solid interface during solidification, which are not considered in present analysis.

## 5.- CONCLUSIONS.

Electron-donor analysis shows that inside liquid aluminum alloys the tendency for Al-Si bonding is more favorable to exist than Al-C. However, the presence of high surfactant halide salts promote wetting, which enhance the Al-C reaction to generate carbonaceous inclusions in the melt.

In the maltese-cross morphologies surfactancy is the cause for silicon absence inside the particles.

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