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The Influence of Crucible Material on Aluminum Composition

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Abstract The freezing point of aluminum is one of the ITS-90 defining fixed points widely used for thermometer calibration. However, long-term investigations have revealed slow temperature depressions of the aluminum freezing temperature and alterations of the metal structure that are probably due to metallic contamination caused by the partial dissolution of crucible material. The objective of this work was to study the interaction of liquid aluminum with graphite and boron nitride in order to select a nonreactive material. Two crucibles made of high purity graphite and boron nitride were filled with Al of 6N5 purity; then, 40 melting-freezing cycles were carried out. The total time of contact between aluminum in the liquid phase and the crucible was 240 h. After that, the composition of Al, graphite, and boron nitride was studied and the results were compared with the analysis of the initial samples. The Al ingot in contact with boron nitride was found to be contaminated by boron.

Keywords Aluminum · Boron nitride · Freezing point · Graphite · Interaction

1 Introduction

International comparisons have revealed significant differences between fixed-point cells of different origin; also, results obtained in different laboratories often fail to coincide. For example, the results of the CCT-K4 comparison indicate that the

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participating aluminum freezing point cells vary by as much as 6.4 mK. It is impossible to establish the main reason for the behavior, but contamination by the crucible material cannot necessarily be excluded. Graphite is traditionally used for the cells, but boron nitride may also be considered a prospective substance because of its chemical inertness; the fact that BN and carbon have the same types of crystal lattice facilitates the comparison of their properties. In our study, we tried to investigate the interactions of liquid aluminum with hexagonal boron nitride and graphite.

All chemical processes in “solid–liquid” and “solid–gas” heterogeneous systems originate with reactions on the surface of the solid body. The surface of a solid is a very complicated form with properties that are usually significantly different from those of the crystalline material as a whole. The distortion of the crystal structure at the surface and interruption of interatomic bonds result in the appearance of surface active sites, with chemical characteristics and features that may differ from the bulk crystal, which play the main role in initiating chemical reactions at the surface.

2 Boron Nitride Properties

In the nitride structure, atoms of low electronegativity (B, Al, Ti, etc.) are surrounded by nitrogen atoms of relatively high electronegativity, resulting in a concentration of electron density mainly in the nitrogen atoms. The latter feature is typical for metal oxides; since the electronegativity of nitrogen and oxygen differ insignificantly (3.0 for N and 3.5 for O atom) [1], one may expect the main properties of oxides and nitrides to be similar. The properties of oxide surfaces have been very well investigated during the last 50 years but nitrides still remain a poorly studied object.

Boron nitride is a binary compound, consisting of equal proportions of boron and nitrogen. The empirical formula is, therefore, BN. Boron nitride is isoelectronic to the elemental forms of carbon, and isomorphism occurs between the two species. That is to say, boron nitride possess three polymorphic forms; one tetrahedral-analogous to diamond, one hexagonal-analogous to graphite, and one analogous to the fullerenes. Boron nitride has been considered to be largely chemically inert and not wetted by many molten materials (aluminum, copper, zinc, iron, etc.).

The surface structure of boron nitride can be schematically represented as

$$\cdots\text{–N}^{\delta-}\text{–B}^{\delta+}\text{–N}^{\delta-}\text{–}\cdots$$

where $N^{\delta-}$ and $B^{\delta+}$ are the surface Lewis acid sites. In reality, we are always dealing with a spatial structure, but all surface sites of one and the same type are identical to each other; the atoms from the inner layers do not directly participate in surface reactions so, such an approach seems to be correct for further consideration.

Adsorption of water is the principal process taking place on the surface of solids in contact with the atmosphere. The angle between the O–H bonds in the water molecule is 104.5° [2], each O–H bond has a dipole moment because of the concentration of electron density in the oxygen atom, so electrostatic interaction with nitride surface sites should orientate water molecules during the first stage of reaction. The second stage is characterized by the breaking of the O–H bond, proton transfer to the $N^{\delta-}$

site, and formation of B–OH and B_2–NH surface species. This type of interaction is usual for oxides, but, at the boron nitride surface, it may be accompanied by a further hydrolysis reaction [3,4]:

$$B_2\text{–NH} + H_2O \rightarrow B\text{–OH} + B\text{–NH}_2$$

The existence of boron nitride surface hydrolysis was confirmed by Arber and Urch [5]. New hydrogen-containing surface species reveal themselves as active sites for the absorption of coordinately-bonded water molecules; further water absorption results in the formation of multi-layer water covering the surface. The binding energy of water molecules decreases in every additional layer, so a few forms of adsorbed water removable at different temperatures exist on the BN surface [3].

Heating a boron nitride sample up to 570 K under vacuum or in a dry, inert atmosphere leads to the removal of all adsorbed water from the surface. Further heating to 770–870 K causes the destruction of the B–OH, B_2–NH, and B–NH_2 species, i.e., at temperatures near the Al melting point (933.473 K), boron nitride surface returns to its initial active state. The difference in the energies of B–N and Al–N bonds is not very large (385 and 360 $\text{kJ} \cdot \text{mol}^{-1}$, respectively) and the electron configurations of Al and B valence shells are identical ($2s^2\ 2p^1$ for boron and $3s^2\ 3p^1$ for aluminum), so the interfacial interaction between Al atoms and $N^{\delta-}$ species seems possible. The diffusion of boron into aluminum may also exist.

These assumptions were partially confirmed in [6], where the wettability and interfacial reaction between liquid aluminum and boron nitride were investigated by the sessile drop method, electron probe microanalysis, and X-ray diffraction. The results showed that the interfacial reaction and diffusion of liquid aluminum on the BN ceramic surface promote wetting of the ceramic. Interface analysis showed that liquid aluminum can react intensely with boron nitride at high temperatures, and there exists a nitrogen-rich layer on the aluminum surface and an excess of boron on that of the ceramic. After the experiment at 1,435 K, the surface of the reaction layer was completely covered by aluminum nitride. At lower temperatures near the Al freezing point, the reaction velocity should decrease, but it may still occur.

3 Graphite Properties

In the graphite structure, each carbon atom possesses a trigonal sp^2 orbital hybridization and the π-electrons are delocalized across the hexagonal atomic sheets of carbon atoms. Thus, in contrast to the partially ionic character of the B–N bond in boron nitride, each carbon atom in the graphite structure is covalently connected by three localized σ-bonds and one delocalized π-bond to three other surrounding carbon atoms. The different atomic layers in the graphite structure are not covalently bonded to the surrounding layers, but they are instead connected by a weak van der Waals interaction. Therefore, the bond between the layers can be easily broken and the surface of an ideal graphite crystal represents an infinite plane, in which the electron density is uniformly distributed, so the surface has no defined active sites. In a real, finite crystal, the atoms in the corners (1, 3 in Fig. 1) and at the edges (2), as well

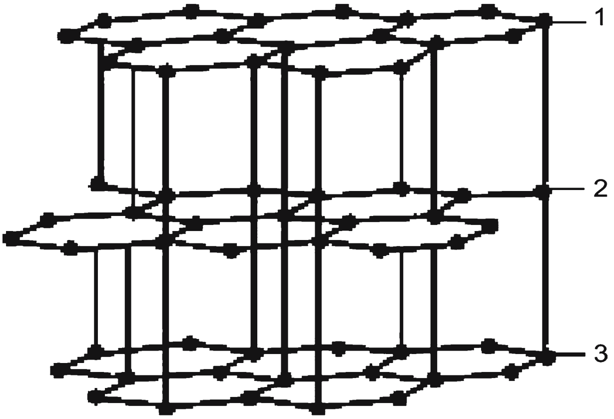

Fig. 1 Graphite structure

as the atoms at crystal structure dislocations, should have at least one free valence with an unpaired electron making this atom chemically active. However, the number of these atoms is relatively small; therefore, graphite is characterized by a rather low chemical activity by contrast with amorphous carbon, which is a good adsorbent and can dissolve in many molten metals.

It is traditionally accepted that there is very poor wettability between solid carbon and liquid aluminum, and that solid carbon is practically insoluble in liquid aluminum. The energy of the C–C bond in the graphite structure is not well defined, but is considered to be approximately $600\,\mathrm{kJ \cdot mol^{-1}}$. The Al–C binding energy is $184\,\mathrm{kJ \cdot mol^{-1}}$; therefore, the interaction between graphite and liquid aluminum seems to be possible only at very high temperatures near the Al boiling point (2,792 K). Contemporary investigations [7] also confirm this; however, reactivity between liquid aluminum and carbon fiber of irregular structure has been discovered at 950 K [8].

4 Experimental Results and Discussion

In our experiment, we used two Al samples of 6N5 purity in the form of cylinders (length of 4 cm, diameter of 1 cm) and two crucibles: one from hot-pressed hexagonal boron nitride, the other from Isostat DE24 graphite with a total ash content of 5 ppm. The crucibles were separately annealed at 1,023 K for 6 h in vacuum with a single intermediate treatment of 5 min in pure oxygen at a pressure of 5 kPa.

The annealing procedure revealed boron nitride ceramics to be rather good water adsorbents (15–20 mg of water per 1 g of BN). Adsorbed water existed on the surface in differently bonded forms: weakly bonded water could be removed by evacuation at 323 K, but full removal occurred only at temperatures near 520 K. The adsorption process was reversible-exposure in air for a few hours returned the ceramics to their initial state. During the first annealing, water vapor coming out of the crucible surface captured BN dust, which then condensed together with water on the cool parts of the annealing tube. The dust flow disappeared only after the fourth annealing. Due to these

Table 1 Analysis of the aluminum sample from the boron nitride crucible

Element	Content in boron nitride (mg/kg) (GIREDMET)	Content in aluminum sample (mg/kg)	
		Before contact with boron nitride (Commissariat à l'Energie Atomique)	After contact with boron nitride (GIREDMET)
B	BASIS	0.0025	9
Ca	10	0.012	0.01
Cl	6	0.0033	0.4
Co	4	0.0005	<0.01
Cr	600	0.035	<0.03
Cu	30	0.060	<0.1
F	10	<0.025	0.02
Fe	200	0.010	0.3
K	7	0.015	<0.01
Mg	400	0.012	<0.007
Mn	50	0.025	0.03
Mo	7	0.007	<0.02
Na	3	0.010	<0.010
Ni	200	0.007	<0.08
P	10	0.0008	<0.01
S	5	0.010	0.2
Si	200	0.065	<0.5
Sr	2	<0.001	<0.03
Te	40	<0.002	<0.02
Ti	200	0.045	<0.03
V	0.9	0.007	<0.01
Y	3	<0.0008	0.02
Zn	<0.4	<0.001	0.8

circumstances, some measures to exclude the occasional contact of molten metal with adsorbed water have been taken.

After annealing, the crucibles with the added Al samples were placed in separate silica glass sheaths that were then arranged in silica glass tubes connected to vacuum and to the argon supply system. Then, 40 "melting–freezing" cycles were carried out during which the metal was overheated by no more than 5 K. During each cycle, the metal remained in the liquid phase for approximately 6 h, so the total time of contact between aluminum in the liquid phase and the crucible material appeared to be 240 h. In order to avoid contact between molten aluminum and adsorbed water, the samples were heated under vacuum up to 870 K at the beginning of each cycle and further heating took place in high-purity argon (99.999% Ar) at a pressure of 0.01 atmosphere. Also, evacuation for 1 h at a temperature exceeding the Al melting point was performed during the first cycle to remove dissolved gases from the metal.

Table 2 Analysis of the aluminum sample from the graphite crucible

Element	Content in graphite (mg/kg) (GIREDMET)	Content in aluminum sample (mg/kg)	
		Before contact with graphite (Commissariat à l'Energie Atomique)	After contact with graphite (GIREDMET)
Ba	3	<0.001	<0.03
Ca	0.8	0.012	0.01
Cl	0.2	0.0033	0.2
Cu	0.4	0.060	<0.1
Fe	0.6	0.010	0.3
K	0.3	0.015	<0.01
Mg	200	0.012	<0.007
Mo	0.8	0.007	<0.02
Pt	300	<0.001	<0.04
S	0.1	0.010	0.2
Si	40	0.065	<0.5
Sn	0.6	0.005	<0.03
Ti	5	0.045	<0.03
V	2	0.007	<0.01
Zn	9	<0.001	0.6

The initial composition of the aluminum samples was analyzed by Shiva Technologies Europe and by Commissariat à l'Energie Atomique, and the final analyses were carried out by the Russian Institute of Rare Metals (GIREDMET). In all cases, mass spectrometers equipped with glow discharge ion sources (MS–GD) were used. Unfortunately, the content of carbon and nitrogen was not measured in all analyses and the information about the behavior of these important elements remained unknown. In the aluminum sample exposed to the boron nitride crucible, the concentration of boron increased from an initial 0.0025–9 ppm. This is contrary to the results of [6] obtained at higher temperature. It appears probable that boron transfer into aluminum occurs at temperatures near the Al freezing point.

The main results of the analysis are presented in Tables 1 and 2. We have chosen for further consideration only the significant contaminants from the crucible material; the influence of other elements can hardly be estimated because of their low content, which was below the detection limits.

The results of the analysis revealed contamination of the Al samples by B, Cl, F, Fe, S, Y, and Zn. The content of Ca, Cr, K, Mg, Mn, Na, Ni, Pt, Ti, and V remained almost stable, and the behavior of Ba, Co, Cu, Mo, Si, Sn, P, and Te was not well defined because of different analysis sensitivity. Unfortunately, at the present time, we have no opportunity to produce a correct estimation of the resulting change in the aluminum freezing point temperature because of the deficiency of data for calculation; this question is currently under study.

5 Conclusion

The results of our study revealed reactivity between boron nitride and molten aluminum at temperatures near the Al freezing point. Also, the adsorption of relatively large amounts of water (and, probably, carbon oxides, ammonia, hydrocarbons, etc.) by BN surface active sites can be an additional source of contamination, complicating the cell preparation procedure. Reactivity between liquid Al and B, Cl, F, Fe, S, Y, and Zn compounds present as contaminants in the crucible material was discovered; other elements and compounds appeared to be mostly insoluble in aluminum. The poor adsorption properties of graphite, and the probable absence of its reactivity with liquid Al, allow us to conclude that high-purity graphite free from contaminants able to interact with liquid aluminum remains the only material suitable for Al freezing point cells.

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