Sp² Carbon Embedded in Al-6061 and Al-7075 alloys in the form of Crystalline Graphene Nanoribbons

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Abstract

Electrocharging assisted process has been used to incorporate carbon in Aluminum 6061 and 7075 alloys ensuing significant improvements of the ultimate tensile strength, hardness, and electrical conductivity. This work investigates the presence of carbon, its structure, carbon-metal bonding, surface characterization and dispersion of carbon incorporated in Al alloys by electrocharging assisted process. Networks of Graphene nanoribbons with 3D epitaxy and preferred orientation along the <110> and <112> directions of Al are evident by transmission electron microscopy and spectrum imaging of the C-K edge electron energy loss spectra. X-ray photoelectron spectroscopy and Raman scattering corroborate sp² carbon in Al-6061, and hybrid sp²-sp³ in Al-7075 with added carbon. Kelvin probe force microscopy substantiates the presence of carbon in the Al matrix. Phonon density of states derived from first-principles calculations predicts C-Al Raman active modes whilst density functional theory indicates covalent bonding between carbon and Al. This method of incorporation of graphene nanostructures in metals with strong carbon-metal bonding can open up new avenues for incorporation of sp² carbon structures in other materials.

1. Introduction

Extending the lifetime, strength and electro-thermal properties of metallic alloys by introducing novel, environmentally friendly and cost effective processing techniques are crucial for strategic advancement, replacement of aging infrastructure and for the development of new technologies in the electronics industry. Conventional uses of many of these alloys are related to lightweight structures, power grids, electronics, and aerospace and naval vessels. With the advent of nanotechnology and nano-electronics the role of metals is becoming more diversified than it has ever been often requiring functionalization for enhanced electrical-thermal, catalytic and optical

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properties. One of the promising candidates considered in such cases is the incorporation of carbon in metals. Carbon nanostructures, such as graphene, carbon nanotubes (CNT), nano-diamond and thin layer graphite have received much attention in the last decade for their superior properties in mechanical and electronic applications. Although historically carbon inclusion in steel was a major player in the last century's global development by improving the hardness, strength and anti-corrosion properties of iron, similar approaches have failed in case of many other metals like Cu, Ag and Au. In such metals the solubility of carbon under normal materials' kinetics is negligible, in the low ppm level [1]. Therefore, investigations of the role of carbon on the electrical, mechanical and anti-corrosion properties of these metals had long been hindered by traditional metallurgical approaches. Presently, many modern processing techniques are being developed in place of conventional methods to embed carbon nanostructures into metal-matrices with impressive results. Significant improvement of mechanical, electrical and optical properties have been observed in copper[2] and silver[3] containing carbon nanostructures. However, many of these methods produce weakly bound metal-carbon bonding by van-der-Waals forces and are not suitable for large scale production.

In the case of aluminium, preserving the nanostructure of carbon with sp^2 bonding and ensuing metal-carbon bonding in the aluminium matrix without the formation of Al_4C_3 are great challenges aside from solubility. Some examples of carbon network incorporation in aluminium are: incorporation of CNT and graphene by ball milling [4, 5], chemical vapour deposition (CVD) [6], friction stir [7], cold spraying [8] plasma spraying [9, 10], and high-pressure torsion method combined with ball milling [11]. Cold spraying, plasma spraying and friction stir of Al with CNT produced Al_4C_3 phases which are believed to be responsible for higher elastic strength, Young's modulus and hardness. Such CNT based metals processing require multiple steps creating more complexity. Interestingly, secondary carbide phases in graphene-Al as well as in single wire nanotube-Al nanocomposites have been reported to be responsible for reduced strength and hardness [12, 13]. Therefore, the role of carbides on mechanical properties is dependent upon the synthesis method, processing temperature, and precipitation and evolution of the microstructures in and between grains. Furthermore, the formation of Al_4C_3 compromises the high electrical and thermal conductivities that are possible by the incorporation of sp^2 carbon network in the metal matrix. In the case of ball milling, the drawbacks are the long ball milling time required and high density of defects which produce mostly sp^3 carbon [4, 14]. Therefore, a single step processing involving strong bonding between the metal and carbon with enhanced

mechanical and electro-thermal properties by maintaining high percentage of sp^2 bonding of the carbon is an attractive goal for many technological applications.

From that perspective and in order to simplify mass production of carbon incorporation in metals, Third Millennium Materials LLC, developed a novel method of incorporating dispersed nanostructured carbon in a metal matrix that we term “electrocharging assisted process of bulk metals”. In this process, particles of activated carbon of 20-50 μm are added to the molten metal in an inert environment followed by the application of a high current to the mixture. Although the mechanism and kinetics of the process are not fully understood, it is assumed that the high current creates ions, both in the metal and the activated carbon particles, and electrons that can react and bond to each other. The metals containing carbon produced by this process are called "Covetics". Applying this technique, different metal-covetics of Al, Cu, Au, Ag, Zn, Sn, Pb and Fe have been produced with nanostructured carbon. In the case of Ag with carbon, termed Ag covetic, 3D epitaxial carbon network was observed [15]. The stability of these carbons in the metal lattice has been verified by cycles of re-melting and solidification, indicating that atomic bonding exists between the carbon and the metal rather than simply forming a composite with trapped carbon inside the molten metal. The properties of these materials are just beginning to be investigated. Promising application areas of such materials include high strength lightweight materials for building aerospace and naval vessels, better electrical and heat conduction in electronics and wirings, and longer lifetime in corrosive environment. Besides, thin films deposited by PLD using bulk copper covetic as target have shown to be potential candidates as transparent electrodes to replace expensive ITO [16].

In case of aluminium, commercially available Al-6061 and Al-7075 alloys have been doped with different carbon concentrations to make Al-covetic samples. These covetics are named after their nominal weight percentage during mixture in the molten metals, i.e., Al-6061 cv 3%, stands for 3 weight percent C added to Al-6061 molten metal during the covetic process. Since pure aluminium is expensive, prone to oxidation and corrosion, and not useful for most industrial applications, studies of widely used commercial aluminium alloy series are useful for practical applications keeping in mind that many body alloy systems often complicate the analysis of the structure and phases. Previously reported mechanical studies of these Al-covetic samples of Al-6061 and Al-7075 have shown remarkable improvements [17]. Namely, the ultimate tensile strength increased by 40% and hardness increased over 30% for 5% C in Al-7075 compared with pure Al-7075 [18]. Also, adding carbon to Al-6061 to make Al-6061 cv 3% improved the tensile

strength and hardness of as-extruded Al-6061 cv 3% compared to pure as-extruded Al-6061 by 23-30% and the electrical conductivity increased by 43% [19]. Thus, adding C improved the mechanical and electrical properties of the alloy in addition to the already high weld ability and anti-corrosion properties of the parent alloys.

The above mentioned improvements necessitate detailed investigation of the carbon incorporation in the matrix of Al-6061 and Al-7075 covetics in order to understand the role of C on the properties. In this paper, we focus on the structure, type of C-C atomic bonding, dispersion of the carbon, and possible bonding between carbon and aluminium. The presence of crystalline carbon nanostructures was confirmed by transmission electron microscopy (TEM). Electron energy loss spectroscopy (EELS) mapping showed nanoribbon like features having sp^2 carbon. Raman mapping confirmed sp^2 carbon in nanoribbon form with small contributions of sp^3 carbon, and with strain. X-ray photoelectron spectroscopy (XPS) was used to determine the bonding characteristics of the carbon and relative concentration of the elements. Further investigations by Kelvin probe force microscopy (KPFM) and atomic force microscopy (AFM) confirmed the presence of carbon on the covetic sample surface. Structural characterization for grain size, strain and presence of secondary phases in these samples was studied by X-ray diffraction (XRD). Density functional theory (DFT) calculations predict bonding between C and Al at the edges of graphene nanoribbons (GNR) and at carbon-vacancies in the graphene-aluminium interface due to the competition between the diatomic Al-Al and Al-C binding energies.

2. Results

2.1 Observation of crystalline graphene nanoribbon in Al covetics

Folded ribbon-like structures, similar to graphene nanoribbons and nanosheets [20-22], were observed in Al-6061 cv 3% by high angle annular dark field (HAADF) in TEM (Figure 1). As the intensity of TEM images in HAADF mode depends on the sample thickness and the atomic weight of the elements in the area, the variations in contrast in Figure 1 a) suggest that the ribbon-like structure marked by arrows corresponds to light elements such as carbon. To confirm the presence of carbon, EDS mapping was acquired for different elements like C, O, Mg, Si and Al from the rectangular area in Figure 1 a). The elemental maps show slightly higher concentration of carbon and oxygen in the folded structure (Figure 1 b) and c)). The other elemental maps from the alloying dopants (Mg, Si, etc.) showed uniform contrast in this region.

However, since the interaction volume in EDS is much larger than the spot size it limits the resolution to distinguish individual ribbon structures. Furthermore, it is difficult to determine the exact thickness of the ribbon-like structure. Multiple scans with similar EDS mapping of the C, Al, O, Mg, Si, etc. were carried out in upper and lower positions, other than the shown purple box, along this ribbon-like regions and sheets. In every case, higher carbon concentrations were detected in this folded region. The black regions, above and below the ribbon-like structure, correspond to secondary phases such as Mg_2Si and CuO . The ribbons and sheets appeared in other grains of the Al alloy and in some cases they even had higher concentration and were crystalline with an epitaxial orientation with the Al lattice as shown below.

Figure 1. STEM Images with elemental mapping. a) High angle annular dark field (HAADF) image of folded ribbon-like regions (arrows) in Al-6061 cv 3%. b) O-K α and c) C-K α EDS mapping of the box region of $1\ \mu\text{m} \times 1\ \mu\text{m}$ area in a) showing higher presence of carbon and oxygen in the ribbon-like structure.

Figure 2. TEM images and selected area diffraction pattern of Al-6061. a) (111) electron diffraction pattern of Al-6061 cv 3% from the left region in b). The hexagonal bright spots correspond to the Al $\langle 220 \rangle$ spots. The weak spots, labelled 1 and 2, in the inner circle are due to the $\langle 10\bar{1}0 \rangle$ reflections on the (0001) plane of crystalline graphite. b) Bright field TEM image of the sample. c) and d) dark field (DF) TEM images using weak spots 1 and 2 in a), respectively. e) Diffraction pattern from the upper right area in b) showing a broad ring corresponding to amorphous carbon.

Evidence of 3D epitaxy of carbon in Al is obtained from TEM electron diffraction patterns that show the presence of a spot pattern that does not correspond to Al or Al_4C_3 . Namely, weak spots, such as the ones labelled 1 and 2 in Figure 2a), are close to $\langle 10\bar{1}0 \rangle$ reflections of graphite and indicate a preferred orientation with respect to the Al lattice (bright spots). The weak spots 1 and 2 are superimposed on a weak and broad ring indicating that some of the carbon is amorphous. The inter-planar distances derived from the weak spots are 0.205 nm , which closely agree with the $\langle 10\bar{1}0 \rangle$ interplanar distance of 0.2127 nm in the basal plane of graphite with $\sim 3.3\%$ compressive strain in the graphitic regions. The strain is probably introduced by the lattice

mismatch between graphite and the Al host lattice as was previously observed in Ag cv 3% and 6% [15]. The schematic in Figure 3 shows the epitaxial relation between the (111) plane of Al and the (0001) plane of graphite. Figure 2 c) and d) show dark field images obtained using, respectively, spots 1 and 2 in Figure 2 a). These images show small crystals of graphitic regions that are aligned along a preferred $\langle \bar{1}\bar{1}2 \rangle$ direction in the lattice of aluminium. Furthermore, all these small crystallites have the same orientation with respect to each other and to the Al matrix, i.e., they have an epitaxial relation with aluminium. Moreover, these small graphitic regions form along lines starting at the interface between the Al grain and a particle of activated carbon (right region in Figure 2 b), c) and d)). The diffraction pattern of the amorphous carbon is presented Figure 2 e).

Figure 3. Schematic of epitaxy of C in Al. Schematic showing the epitaxial relation between graphite and the (111) plane of Al corresponding to the pattern observed in Figure 2 a). There is a 13% mismatch between Al low potential sites and C-C distance in graphene.

2.2. sp^2 bonding of C in covetics

EELS spectrum imaging confirmed the presence of sp^2 bonding in Al covetics which is similar to the activated carbon used as source in the process of conversion to covetics. Namely, a sharp edge at ~ 284 eV is observed in the C-K edge spectra in Figure 4 for Al-6061 cv 3% and activated carbon indicating transitions of C 1s electrons to π^* antibonding unoccupied orbital.

Figure 4. EELS spectra of Carbon. C-K edge profile after background subtraction presenting the sp^2 character of a) Al-6061 cv 3% and b) the activated carbon used as source.

Figure 5. EELS mapping of GNR. a) HAADF image of Al-6061 cv 3% TEM sample. EELS spectrum image was acquired from the green rectangle region labeled as Spectrum Image. The yellow rectangle labeled Spatial Drift was used to correct for any drift of the sample during the data acquisition. b) False color map of the C-K edge showing preferential distribution of carbon in ribbon geometry. The bright regions have higher concentration of carbon compared to the dark regions. The dark regions in a) appear whitish in the C-K edge profile for carbon enriched regions. False color maps of the c) Al-K edge and d) O-K edge where both Al and O present uniform distribution.

The C-K edge map obtained from the EELS spectrum image shows the presence of nanoribbons varying in width from 20 nm to 40 nm (Figure 5). In HAADF, atoms with low atomic mass appear dark because of lower scattering of electrons compared to the heavier elements. C is the lightest element of all in this case because of its atomic mass of 12.011 compared to 26.98 for

Al. The whitish regions in Figure 5 a) correspond to the dark regions in Figure 5 b), both indicating less carbon present in those regions. Similar ribbon-like features are present in Figure 2 a) from another TEM sample. In contrast, the maps from the Al-K and O-K edges show fairly uniform contrast in the same area (Figure 5 c) and d), respectively).

Figure 6. Raman spectra. Raman spectra from the pure Al-6061, activated carbon, Al-7075 cv 3%, Al-7075 cv 5% and Al-6061 cv 3%. G and D-peak positions are shown by arrows. Intermediate modes and high wave number modes are not clearly visible but only a weak signal in Al-6061 cv 3% and Al-7075 cv 5% in this range of wave numbers is apparent.

In order to characterize the form, along with the distribution, of the GNR and other forms of carbon in the covetic samples, Raman spectra were obtained since Raman is a reliable and non-destructive technique that has been used extensively to characterize different forms of carbon [23-26]. The Raman spectra from the Al-covetic samples in Figure 6 show sharp and strong graphitic (G and D) peaks which are not observed in the reference samples with no C (bottom spectrum in Figure 6). The G-peak at $\sim 1585 \text{ cm}^{-1}$ is due to the single photon emission process known as first order Raman scattering produced by tangential stretching (E_{2g}) mode of the graphite plane [23] while the D-peak at $\sim 1350 \text{ cm}^{-1}$ is related to second order Raman scattering involving one phonon double resonance for sp^2 carbon. The D-peak is active when there are defects in the hexagonal graphite structure and results from in-plane vibrations[27]. In graphitic carbon there are also a broad band at $\sim 3250 \text{ cm}^{-1}$ which is the $2D'$ ($2LO$ mode), a band at $\sim 2950 \text{ cm}^{-1}$ the $D+D'$, also called, $2D$ peak and a peak at $\sim 2700 \text{ cm}^{-1}$ resulting from a two phonon

Raman process dependent upon the π -band of the electronic structure of graphite [28]. However, besides the G and D peaks, the spectra in Figure 6 do not show clear evidence for other graphitic peaks but rather weak and broad intensity in these regions of high wavenumbers are observed which are similar to spectra from GNR and graphene sheets. The ratio of integrated intensities of the D and G peaks (I_D/I_G) indicates some disorder in the graphite and is inversely related to the graphite crystallite size [29]. The graphitic crystallite sizes, L_a , were estimated from the following formula in terms of the laser wavelength, λ_{laser} , and (I_G/I_D) ratio:

$$L_a \text{ (nm)} = (2.4 \times 10^{-10}) \lambda_{\text{laser}}^4 (I_G/I_D) \quad (1)$$

For the covetic samples, the average width of the graphitic regions derived from eq. (1) was 8-11 nm for all covetic samples. The FWHM of the D peak in the covetic samples is $\sim 200 \text{ cm}^{-1}$ and indicates a high defect concentration.

2.3. Surface potential mapping

AFM height, phase, and KPFM images (Figure 7, Figure 8, and Figure 9) reveal differences in the microstructure of the Al-6061 and Al-7075 samples due to compositional variations. Variations in the phase images were observed from both the carbon (dark features approximately 20 nm in size) and other phases within the alloys, such as Mg_2Si and Al-Fe-Cu as found in XRD and EDS mapping. In Al-7075, the concentrations of Zn, Fe and Cu are higher compared to Al-6061, further complicating the analysis.

Figure 7. AFM and KPFM of Al-6061 cv 3%. a) AFM height b) AFM phase and c) KPFM potential mapping of Al-6061 cv 3% sample. There is a correlation of the dark regions in b) and c) suggesting that these regions contain carbon because of the lower work function of carbon compared to the Al-matrix.

Figure 8. AFM and KPFM of pure Al-6061. a) AFM height b) AFM phase and c) KPFM potential mapping of pure Al-6061 sample of the same region. The phase and KPFM images show clear differences compared to the Al-6061 cv 3% in Figure 7. Potential mapping is uniform in the whole scanned region unlike the covetic samples.

Figure 9. AFM and KPFM of Al-7075 a) AFM phase and b) KPFM potential mapping overlaid on the topographic image of the Al-7075 cv 5% sample showing correspondence of the dark regions in both figures which suggests formation of carbon ribbons. In b) the lower potential regions indicate a phase of higher conductivity. Also, the KPFM map shows a directional preference of lower potential regions which agrees with the phase image.

KPFM is thus useful for distinguishing carbon from the alloying elements (i.e. Al, Zn, Mg) since carbon and the AFM tip coating (Pt) have similar work functions. As a result, the surface potential is relatively low for the regions containing C. Figure 7 shows 5 μm x 5 μm height, phase and KPFM maps of the Al-6061 cv 3%. The dark features present in the phase images correspond to the relatively low surface potential areas. Reference samples of these alloys without carbon doping were also investigated under the same conditions but did not show

contrast in both phase and potential mapping (as expected from a uniform alloy) (Figure 8). Low surface potential regions were also observed for the Al-7075 cv 5% sample shown in Figure 9 and similar results were found for the Al-7075 cv 3% samples (not shown). The AFM tip was set at a distance of ~ 10 nm from the surface for the KPFM scans in order to achieve a balance between high sensitivity to the surface potential while also minimizing influence in the signal due to topographic variation in the sample. Thus, the fly-height decreases the spatial resolution to some degree and therefore the individual GNR-like features cannot be clearly distinguished and only clusters of them can be observed in Figure 7 and Figure 9.

2.4. Quantification and bonding of carbon from XPS

XPS showed that the percentage of carbon in the covetic alloys is lower than the nominal values. High carbon content was observed on the surface of all samples originating from hydrocarbon contaminants with significant amount of sp^3 carbon. Similarly, aluminium oxide was evident in the surface region of the samples. While the C signal decreased with sputtering time and reached some equilibrium value after about one minute (for the pure Al alloys, not shown) and four hours (for the Al covetics) of sputtering time, the oxygen signal continued to decrease even after eight hours of sputtering indicating that some oxygen is incorporated during the addition of carbon in the covetic samples (See Figure 10).

Figure 10. XPS depth profile of the Al-6061 cv 3%. Atomic percentage of the Al, C and O depth profile is plotted as a function of sputtering time. On the surface, high percentage of carbon was observed due to hydrocarbon contamination. Ar-sputtering of the samples for extended period gave stable values of around 3 at. % carbon.

Figure 11. High resolution XPS spectra a) C 1s after 1 hour of sputtering of Al-6061 cv 3% showing mostly sp^2 carbon with weak signal in the lower binding energy region possibly from Al-C bonding. b) C 1s of Al-7075 cv 5% under similar conditions as a) showing the presence of hybrid sp^2 (283.8 eV) and sp^3 (284.8 eV) bonding separated by 1 eV. The overlap of two peaks with different bonding results in peak broadening and contributes to the different degree of asymmetry at higher binding energies compared with pure sp^2 and sp^3 bonding alone. Besides the weak peak in the region for Al-C bonding, other weak peaks corresponding to possible formation of C-O, C=O and hydrocarbon are present. c) O 1s from surface of the Al-7075 cv

3% sample clearly showing the presence of two different types of C-O bonding with a broad doublet in the data after 4 sputtering cycles. The data were fitted with C=O (532.3 eV) and C-O (533.3 eV) separated by 1 eV and the envelope fitting combines the contributions from these two components in good agreement with the experimental data.

Besides Al, C and O, other elements of the alloys, such as, Si, Cu and Zn were detected by XPS as expected from the Al-6061 and Al-7075 alloy specifications. For Al-6061 cv 3%, an asymmetric C 1s peak with a characteristic tail towards higher binding energy, a signature of sp^2 dominant bonding, was observed in the high resolution spectrum as shown in Figure 11 a). The spectrum also shows weak evidence for C-Al bonding centered at 282.7 eV, analogous to that in Al_4C_3 . Comparable spectra were obtained from the Al-7075 covetic series but these samples showed weaker and noisier signal indicating lower C concentration (see Figure 11 b) for the sample with 5% C). Compared to the peak in Figure 11 a) for the Al 6061 cv 3% sample, the C 1s peak in the Al-7075 cv 5% sample is much broader. The maximum intensity of this peak is at ~284 eV which indicates a mixture of sp^2 and sp^3 bonding. The broad tail in the region of high binding energy is an indication that some C atoms could be bonded to other atoms (other than C), such as C-O, carbonyl groups (C=O) and carboxylic groups (C-O-O-H). However, due to the noisy signal from XPS quantification of the results in terms of components of the different C-oxides is not possible. Additional evidence for C-O bonding, however, can be extracted from the O 1s spectrum as seen in Figure 12 c) which shows a broad peak that can be fitted to two C-O bonding types; namely, C=O at 532.3 eV and C-O at 533.3 eV, and separated by 1 eV from each other as expected. The fit agrees fairly well with the experimental data for the O 1s peak. O 1s from Al-7075 cv 5% (not shown) also exhibited similar characteristics. Comparable XPS data for C 1s and O 1s were previously found in bulk GNR [30]. In all Al covetic samples, there was overlap of peaks with binding energies corresponding to Zn, Mg, Fe, Si and Cu (not shown) present in the parent alloys making it difficult to quantify the concentration of these elements in absolute values. Nonetheless, the concentrations of elements, other than Al, in Al-6061 samples were less than 2%, as expected from Table 1.

Table 1. Elemental composition (wt. %) of aluminium series.

Element	Al-6061	Al-7075
Cr	0.04-0.45	0.18-0.28
Cu	0.15-0.4	1.2-2
Fe	0.7	0.5
Mg	0.8-1.2	2.1-2.9
Mn	0.15	0.3
Si	0.4-0.8	0.4
Ti	0.15	0.2
Zn	0.25	5.1-6.1
Al	Balance	Balance

The relative concentration of Zn and Cu in Al-7075 are more prominent compared to Al-6061 although the Zn concentration in Al-7075 was lower than the nominal values. Therefore, the carbon in the covetics was quantified with respect to aluminium and oxygen only, i.e., neglecting the other elements in the alloy. In Al-6061 cv 3%, equilibrium values of carbon were approximately 3 at. % (~1.4 wt.%) , while in Al-7075 covetic samples the concentration was around 1.5 at. % for both nominally 3 wt.% (6.5 at%) and 5 wt.% (10.57 at%) samples.

2.5. Structural characterization

XRD was used to obtain the lattice constants of the samples and to investigate the presence of carbon phases or other impurity phases in the covetics. The spectra from all the samples showed no evidence for any carbon based phases (Al_4C_3) or any of the allotropes of carbon as presented in Figure 12. However, small amounts of secondary phases, such as, Mg_2Si and Fe-Si were found in the Al-6061 samples and Al_2CuMg_7 , and MgZn_2 in the Al-7075 samples. The samples showed polycrystalline spectra with variations in the intensity of the (hkl) reflections indicating some preferred orientation of the grains in the samples. Since there is overlap of some of the peaks for the different phases in the XRD spectra it was not possible to quantify the secondary phases. The lattice parameter, grain size and strain calculated from the positions of the peaks in the spectra were compared to the pure Al alloys with 0% C (Table 2). It is interesting that the lattice constant decreased with increasing C content for both Al-6061 and Al-7075 covetics. Also, the average crystallite size estimated from XRD decreased with increasing C content for Al-7075 but not for Al-6061.

Figure 12. Phase Identification by XRD. XRD spectra of pure Al-6061, Al-6061 cv 3%, pure Al-7075, Al-7075 cv 3% and Al-7075 cv 5% C. Mg_2Si , Mg-Zn and Al_2CuMg_7 phases were observed in Al-7075, and Mg_2Si and Fe-Si in Al-6061. FWHM of the Al-peaks varied with carbon doping but no carbon phase was detected.

Table 2. XRD studies of samples. Lattice parameter, grain size and strain of Al covetics calculated from the XRD

Sample	Lattice Parameter (nm)	Crystallite Size (nm)	Strain (%)
Al-6061 (0% C)	0.405233(2)	146.1(8)	0
Al-6061 (3% C)	0.405121(2)	184.5(12)	-0.0276
Al-7075 (0% C)	0.405518(4)	107.4 (11)	0
Al-7075 (3 %C)	0.405461(7)	82.2(8)	-0.0141
Al-7075 (5 %C)	0.405281 (5)	67.1	-0.0584

2.6. Bonding between C and Al

Similar to the case of Ag covetic considered in our previous publication [15], the stability of Al covetic is a result of strong bonding between individual C and the Al atoms in the interfacial graphene-aluminium layers. DFT based calculations for a 3D epitaxial structure of graphene layers on top of Al (111) planes show that if the interfacial graphene sheet is perfect and contains no defects such as carbon vacancies and/or edge carbon atoms (in graphene ribbon), there is no bonding between individual Al and C atoms at the graphene-Al interface. This is expected since

in perfect graphene all the C atoms have saturated bonds, and the energy needed to break any of these bonds exceeds 3.5 eV which is definitely higher than the Al-C bond energy of 2.78 eV in diatomic Al-C molecule [31]. Therefore, it is energetically favourable for the interfacial carbon and Al layers to stay unmixed instead of forming a carbide phase. However, a direct bonding between C and Al becomes possible when the interfacial graphene layer contains defects such as C vacancies and/or at carbon atoms at the edges of graphene ribbons [32, 33]. In such cases: (i) defects in the graphene sheet cannot be “self-healed,” i.e., under coordinated C atoms have no possibility to attach to other carbon atoms, and; (ii) Al-C bonds, with some Al atoms positioned at the interfacial Al (111) plane (and passivating the carbon dangling bonds), become energetically favourable.

Figure 13. DFT model of Al-C bonding. Relaxed structure of graphene nanoribbons on top of Al (111) –substrate obtained by DFT calculations. Al atoms are shown in blue, C – in grey. The ribbons were created by removing two neighbouring carbon rows from a continuous graphene interfacial layer. The next graphene layer remains nearly undisturbed.

First-principles DFT based calculations indicate that bonding between C and Al at edges of graphene ribbons and at C vacancies (Figure 13) has a covalent character which is similar to the Ag covetic [15]. An interesting feature is that each interfacial Al atom can form more than one bond (two or three) with under coordinated carbon atoms positioned at the ribbon edge, which is related to its three valence electrons. Also, some Al atoms could be displaced from the original Al (111) surface layer to the graphene layer. This is not surprising because the diatomic Al-Al bond energy (2.74 eV) is nearly equal to the diatomic Al-C bond energy (2.78 eV) [31] which means that an interfacial Al atom has no preference to which atom to bond – to another interfacial Al or to under coordinated carbon from the graphene edge. In the typical situation shown in Figure 13, interfacial Al atoms form both Al-Al and Al-C bonds which favours mixing between atoms at the ribbon edges and other defects. This result is not surprising based on the fact that Al and C may form Al_4C_3 which is a stable compound. However, mixing between Al

and C atoms may occur at defect precursors (edges and vacancies) only because breaking C-C bonds in ideal graphene structure is energetically unfavourable. This result explains why graphene ribbons do not completely dissolve in the Al matrix but instead form Al covetic.

2.7. Tensile Strength of Al covetic

The carbon in covetics plays an important role on the mechanical properties of the material as seen in the tensile strength of the Al-7075 covetics in Figure 14 compared to pure Al-7075 with no carbon added. There is an increase in the ultimate tensile strength (UTS) of the samples with added carbon although there is small difference between the samples with 3% and 5% carbon. This is probably because XPS showed almost the same amount of C in both samples. The experiments were repeated several times with a standard deviation of few MPa, which is insignificant compared to the values obtained. However, the hardness measured by nanoindentation and Vickers measurement indicated a higher value for the sample with 5% than 3% carbon [18] . Similar results have been reported for as-extruded Al 6061 covetic with 3 wt.% C which shows a 30 % increase in ultimate tensile strength compared to a pure as-extruded Al 6061 with no C [19].

Figure 14. Increased tensile strength by carbon. Ultimate tensile strength of Al-7075 covetics with nominally 0, 3 and 5 wt. % C showing average values with standard deviations for 3 sets of measurements.

3. Discussion

For pure Al-6061 and Al-7075 with 0% C, no evidence for carbon phases was found in the Raman spectra (see Figure 6). In contrast, the covetic samples presented strong and sharp G and D peaks but no peak for the 2D and 2D' peaks in the high wave number region was observed. Instead, a weak and broad hump like feature was seen in most of the covetic samples. These features, similar to previous studies [29, 34] indicate the presence of graphene-like nanoribbons (GNR) supporting the TEM and EELS studies in Figure 1, Figure 2 and Figure 5. The overlapping of G and D peaks in the Raman spectra also indicates the presence of graphene oxide [35] in agreement with the observation of oxygen in the EELS spectrum imaging (Figure 5) and XPS (Figure 10 and Figure 11) from these samples. The Raman laser spot used to obtain the data was ~ 700 nm in diameter whereas the ribbons' widths are much narrower in the tens of nm range. This results in acquiring Raman signals from many ribbons including the ribbons' edge structures which contain large numbers of broken carbon bonds and probably oxidized carbon. These defects and overall disorder of graphene-like structures suppress the sharp characteristic peaks typical of graphene at high wavenumbers and replace them by overlapping broad features at combinations of the different Raman active phonon modes. The intensity of the G-peak is inversely proportional to the width of the GNR and number of graphitic layers in graphite nanocrystals. In the Al covetic samples large intensity variations of the G-peak were observed. Probing of the maximum of the D-peak in the Raman spectra at many different spots of the samples showed that the carbon has primarily sp^2 bonding as the D-peak was located at ~ 1350 cm^{-1} . sp^2 bonding is also indicated by the sharp C-K edge at 284 eV in the EELS (Figure 4) and the shape of the C 1s peak in the XPS spectra (Figure 11) from these samples. There is also indication of strain due to the lattice mismatch of the C-C interatomic distance in graphene and aluminum's distance between low potential sites on the (111) plane as observed in TEM (Figure 2). Strain changes the interatomic distances of the carbon lattice impacting the vibrational modes detected in Raman. Blue shift of the G-peak in these samples from 1585 cm^{-1} is a sign of a compressive stress. The shift of the D peak in the Raman spectra might also be an indication of multilayer stacking of graphitic layers in these regions [36]. The broad FWHM of the D-peak ~ 200 cm^{-1} and the ratio of the integrated intensities (I_D/I_G) in the range 1.8-2.4 in the Raman spectra suggest a high concentration of defects; such as, edges of the GNR and possibly oxidation.

In case of perfect graphene, the D peak is absent or hardly visible compared to the G-peak intensity resulting in the I_D/I_G ratio to be zero. However, at the edges of graphene sheets the D peak becomes stronger with significant intensity compared to the G and G' peaks. The TEM images obtained from Al covetic samples (Figure 2) show small regions with higher concentration of carbon that form arrays of ribbons along preferred crystallographic directions of the Al lattice starting at the interface between an amorphous carbon particle and an Al grain. These ribbons contain small graphitic crystals with a preferred orientation relative to the Al lattice and similar to Ag covetic [15] with (111) Al // (0001) graphite and $\langle 1\bar{1}0 \rangle$ Al // $\langle 11\bar{2}0 \rangle$ graphite. We believe that when the current is applied, in the process of conversion to covetics, carbon atoms from the activated carbon particles become ionized and bond to each other forming chains and layers of carbon which upon solidification of the aluminum around them get trapped along preferential directions of the Al lattice. These structures become very stable as our DFT calculations show that some of the carbon atoms at either edges of ribbons or next to vacancies bond to Al atoms. Furthermore, the graphene-like ribbons form a network throughout the sample that gives rise to an increase in the tensile strength of the alloy.

4. Conclusion

In conclusion, the presence of sp^2 carbon forming graphitic-like ribbons with preferred orientation with the crystal lattice has been confirmed in samples of Al-6061 and Al-7075 covetics using different characterization techniques. The carbon forms networks of ribbons embedded in the Al-matrix parallel to the $\langle 112 \rangle$ directions of Al and with epitaxial orientation of (111) Al // (0001) graphite and $\langle 1\bar{1}0 \rangle$ Al // $\langle 11\bar{2}0 \rangle$ graphite with a compressive strain of $\sim -3.3\%$ of the graphitic layers. Moreover, the incorporation of C gives rise to a slight reduction of the Al lattice parameter and a decrease in average grain size. Theoretical calculations using DFT indicate that bonding between C and Al occurs at edges of ribbons and next to C vacancies. The carbon network is believed to be responsible for the increase in ultimate tensile strength in these materials as well as previously reported increase in electrical conductivity. These findings show potential for the utilization of these alloys in high strength and electrical conductivity related applications and also demand further consideration of the phase diagrams of insoluble elements at non-equilibrium conditions for novel functionalized alloys unknown today.

5. Experimental details

5.1. Materials synthesis and samples

5.1.1. Al-Covetic synthesis

The samples for this study were obtained from Third Millennium Materials, LLC in Waverly, OH. They were prepared by adding activated carbon particles of 20- 50 micron size to molten Al-6061 and Al-7075 alloys and applying a high dc current to the mixture while stirring to make it homogenous throughout the solution. Carbon in concentrations of 3 wt. % (6.5 at. %) was added to Al-6061, and 3 and 5 wt % (6.5 and 10.57 at. %, respectively) were added to Al-7075. The covetic alloys were compared to pure alloys with no carbon. The Al 6061 samples (with and without carbon) analyzed in this work were cast into 7.5 cm diameter rods which were then as-extruded with exactly the same conditions in the form of 1.25 cm diameter as-extruded rods at a processing temperature of 227° C. For the Al-7075 0% C a high current was applied to the melt but no activated carbon was added which resulted in a small C incorporation in the sample originating from the graphite electrode used to apply the current. The Al-7075 samples were rectangular plates of 1.295 to 1.65 cm thick by 20.32 to 30.48 cm long by 15.24 cm wide as starting material. They were warm rolled at 450 °C at 20% reductions per pass for 5 cycles resulting in a final thickness of 1 mm. The nominal concentrations of the elements in the starting Al alloys in these series are shown in Table 1 [37].

5.1.2. Sample preparation

Small pieces of the covetic and pure metal samples were cut and polished with alumina paper starting with 12 µm, followed by 9 µm, 6 µm, 3 µm, 1 µm and 300 nm particle sizes to remove scratches on the surface and get a flat and smooth surface. After polishing the samples were sonicated in acetone and isopropanol for removal of hydrocarbons and any residue from the polishing paper left on the surface. The same samples were used first for Raman, and KPFM and finally for XPS.

5.2. Characterization of samples

5.2.1. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) data were collected using aluminium mono-chromator source at 14 KV in ultrahigh vacuum in a Kratos AXIS 165 spectrometer. Ultra-pure Ar-gas was

used to sputter away hydrocarbon contamination on the surface. The sputtered area created by the raster at 4kV and 25 mA current was around $7\text{mm} \times 7\text{mm}$. Sputtering of the surface was carried out for 1 hour per cycle for 5 cycles and with a final 3 hour sputtering cycle. Data were acquired after each cycle and were calibrated using the Al-2p peak at 72.6 eV and applying Shirley background subtraction. From the depth profile, the average value of the actual carbon concentration in the material was determined.

5.2.2. X-ray diffraction

X-ray diffraction (XRD) with Cu-K α ($\lambda = 0.154056\text{ nm}$) in a D8 Advanced (Bruker) diffractometer was used to obtain the lattice constant and structure of the alloys and to investigate the presence of any of the allotropes of carbon and other secondary phases. The XRD data were fitted with mixed Gaussian-Lorentzian curves by Rietvelt method using TOPAS-4 software (Bruker).

5.2.3. Transmission electron microscopy

High spatial resolution imaging and microstructure analysis were carried out using a JEOL 2100F field emission TEM/STEM operated at 200 kV with spherical aberration coefficient C_s of 0.5 mm, point-point resolution of 0.19 nm and lattice resolution of 0.10 nm. TEM lamella were prepared either by mechanical polishing with diamond lapping paper with decreasing particle size from 9 to 3 μm until the sample was $\sim 15\text{ }\mu\text{m}$ thick or by electropolishing in a solution of 15:35:4 by volume of nitric acid:methanol:butoxyethanol at a temperature of $-45\text{ }^\circ\text{C}$. The thinned samples were then ion milled at low angle using Ar^+ ions to get electron transparency at an angle of 5° with a voltage of 3 KV and current of 3 mA. EELS was carried out using a Gatan GIF Tridiem post column energy filter for spectrum imaging and electron energy loss spectrometry (EELS) for composition analysis.

5.2.4. Raman

Raman spectra were taken using a Nd:YAG laser (532 nm) with a 100X lens by confocal micro-Raman system from HORIBA Jobin Yvon LabRam ARAMIS. The data were analysed using LabSpec 5 software.

5.2.5. Kelvin probe force microscopy

Scanning probe force microscopy measurements were performed using an Asylum Research Cypher AFM. The probes used in the study (PtSi-FM, Nanosensors) had a spring constant and resonance frequency of approximately 5 Nm^{-1} and 75 kHz, respectively. The tips had a nominal radius of curvature of 25 nm and included a conductive Platinum Silicide coating. Topography, phase, and Kelvin probe force microscopy (KPFM) measurements were made in AC mode with a scan rate of approximately 1 Hz. In KPFM, the difference in work function between the sample and the conductive tip was monitored in order to map surface potential. The KPFM technique was used in the present study to investigate variations in the physical and chemical properties of the covetic materials with respect to the control parent alloys. KPFM images were corrected using a dual pass scan; an initial forward/reverse scan determines the height variations for a given raster, while the subsequent KPFM pass at a defined fly-height ($\sim 10 \text{ nm}$) allows the AFM probe to map the surface potential. However, the fly height used during KPFM results in reduced resolution with respect to the height and phase images.

5.3. Theoretical calculations

In order to investigate the role of different atomic scale and nanoscale features in the epitaxial accommodation of graphene layers and graphene ribbons at the Al surfaces and between layers with [111] orientation, a significant number of different graphene–Al periodic supercells was constructed and their geometries optimized using DFT. We used “slab” supercells (three layers of graphene on top of four layers of Al [111]). A periodic hexagonal supercell with parameters $a = 1.475 \text{ nm}$; $c = 3.010 \text{ nm}$ was used. The value of the parameter a corresponds to ~ 5 lattice constants of the 2D periodic structure in Al (111) plane and ~ 6 lattice constants of the graphene structure, which reasonably takes into account most of the lattice mismatch between the two structures. For slab supercells a vacuum layer was added between slabs of $\sim 1.6 \text{ nm}$ in the c direction which guarantees that different slabs will not overlap. The positions of Al atoms in the lower layer of the slab (opposite to the “free” graphene surface) were fixed. The DFT calculations were based on the generalized gradient approximation (GGA) for exchange and correlation, and plane waves [38]. The GGA functional of Perdew, Burke, and Ernzerhof (PBE) [39] was used, which gives good results for chemisorption of molecules at transition metal surfaces. Projected augmented wave (PAW) scalar relativistic pseudopotentials [40, 41] and the VASP code [42, 43] were used. The energy cut-off for the plane-wave basis was set at 500 eV, and all integrations over the Brillouin zone were done using the Monkhorst–Pack scheme with one to four k points in the relevant irreducible wedge [44]. Inclusion of additional k points was

found to have minimal effect on the total-energy differences of interest. The total number of atoms varied between 300 and 750 atoms for different periodic supercells. For each supercell, all atoms were relaxed until the quantum-mechanical force on each atom became smaller than 0.02 eV Å⁻¹. Most of the calculations were spin-polarized. Activation barriers were calculated using the nudged-elastic-band (NEB) method [45]. In some cases (when the potential energy curve was very steep around the transition state) the adaptive NEB approach was employed [46], because the conventional NEB sampling did not provide satisfactory results. The pre-exponential factors and reaction rates were not calculated for the considered reactions. Although such calculations could be performed [47], they are very difficult and time consuming. Comparison between the activation barriers at different surface sites provides only qualitative information which, however, is quite sufficient for most of the practical purposes.

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