Exploring Covetics

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Abstract
Advancements in nanomanufacturing have made it possible for large amounts (> 6 wt.%) of carbon to be incorporated into metals such as aluminum, silver, copper and others. This method is known as 'electrocharging' where high electric current is applied to the molten metal containing particles of activated carbon and new bond are created. This method was used to create the materials by incorporating activated carbon into the Aluminum alloys 6061 & 7075. This new material is also being termed "covetics". Despite the possibility of this material not being predicted from phase diagrams, the structure remains highly stable after remelting and resolidification. After experimentation it seems that the new covetic aluminum alloys have enhanced properties such as tensile strength, hardness, and electrical conductivity. The materials have been studied through various microscopic and spectroscopic techniques to shed some light into the composition and structure. After testing, it appears the carbon in embedded into the host matrix.

Introduction
Enhancing the properties of metallic alloys by introducing environmentally friendly carbon as well as using cost effective techniques are necessary as the world grows and develops. Society will need to replace aging infrastructure as well as improve technology in the electronics industry. Carbon nanostructures have received a lot of attention in the past decade for its superior properties in mechanical and electrical applications. Advancements in metallurgic approaches have made it possible to embed these carbon nanostructures into metal matrices. Significant improvements of mechanical properties in aluminum have been observed after the carbon has been added. Embedding the carbon into the aluminum alloys has not been an easy task because of the formation of Aluminum Carbide and problems with solubility. Some examples of carbon network incorporation into aluminum are: ball milling, chemical vapor deposition, plasma spraying, and many more.1 The metals used in our experiments were acquired from Third Millennium Materials LLC who used the method of electrocharging. In this process particles of activated carbon of 20 - 50 micrometers are added to the molten metal in an inert environment followed by applying a high voltage current. The mechanism and kinetics are not fully understood, it is assumed that the high current creates ions both of the metal and

[1] Rashkeev, Surgey Et Al. "Carbon." Sp2 Carbon Embedded In Al-6061 & Al-7075 Alloys In the Form of Crystalline Graphene Nanoribbons (n.d.): n. pag. ELSEVIER, 24 May 2016. Web. 20 June 2016.

activated carbon, then reacting and bonding with one another. The stability of these bonds have been verified from cycles of melting and solidifying the alloys to see if the carbon can be removed. Since the carbon could not be removed by this method, it proves there is some sort of atomic bonding between the carbon and aluminum instead of a mixture. The properties of these materials are just beginning to be investigated heavily. Commercially available Al-6061 and Al-7075 alloys have been doped with different carbon concentrations to make the Al-covetic samples. Since pure aluminum is expensive and prone to oxidation and corrosion, these alloys are more practical in applications. However, alloys systems often complicate the analysis of structures and phases. Since other studies have reported an increase in ultimate tensile strength by 40% and hardness by 30% in Al-7075 cv 5% compared with pure Al-7075, there needs to be a detailed investigation on structure, type of bonding, dispersion of the carbon in Al, and the bonding between carbon and Al. This can be done with various types of microscopy such as transmission electron microscopy (TEM) as well as X-ray diffraction (XRD) and certain calculations based off of density functional theory (DFT). To make DFT calculations, special computer software and algorithms were necessary. The program used is called VASP which computes atomic scale materials modelling, e.g. electronic structure calculations and quantum-mechanical molecular dynamics, from first principles. VASP computes an approximate solution to the many-body Schrödinger equation, either within density functional theory (DFT), solving the Kohn-Sham equations, or within the Hartree-Fock (HF) approximation, solving the Roothaan equations.2 This program is useful for determining the lowest energy potential wells with carbon inside of an aluminum lattice structure.

Literature Review

Not many articles have been posted on this subject due to the few amount of groups researching this topic, however there are still some comprehensive articles out there. A group on the east coast from the University of Maryland (and others) posted a paper on covetics in different types of metals instead of just aluminum.3 They explored whether or not the carbon was actually in metal lattice structures, the possible location in the lattice structures, and compared the results from different metals. This was important in determining what type of carbon nanostructures are forming in these metals and whether it is particular to which metal it is in. The same group also posted another article on covetic materials, but instead of focusing on the nanostructure of the carbon in the metal lattices, it focused more on the improved properties in various metal alloys. They looked at the differences in melting point, density, thermal conductivity, electrical conductivity, and strength between a pure sample and a covetic sample. Their research and publications legitimized covetic materials and their possible impact on the modern world.

Results

Due to the short amount of time, the long waiting periods for training on spectroscopy equipment, and the steep learning curve for the VASP simulation program, my results are rather short. In terms of the VASP program, it took a while to get approved for access and learn the

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[2] "Computational Materials Physics » VASP." *Computational Materials Physics » VASP*. Universitat Wein, n.d. Web. 20 July 2016.

[3] Salamanca-Reba, Lourdes Et Al. "A New Type of Carbon Nanostructure Formed Within a Metal-Matrix." (n.d.): n. pag. Naval Surface Warfare Center, Carderock Division, May 2012. Web. 20 June 2016.

commands to use. It took a lot of trial and error to make progress and a lot hours to find small solutions. I was able to run calculations for simple systems such as lattice energies for single atom or diatomic molecules. Here I was able to construct energy versus atomic position diagrams to find the position that corresponds to the lowest energy. By starting with simple systems modeling more complex systems, like carbon in an aluminum lattice, becomes easier. If I had more time I could have potentially done this and received some results pertaining to the aluminum covetic material. XRD experiments were used to obtain the lattice constants of the samples and to investigate the presences of carbon phases or other impurity phases in the covetics. The spectra from all samples showed no evidence for carbon based phases or any of the allotropes of carbon as shown in figure 1. However, small amounts of secondary phases were found in the samples.

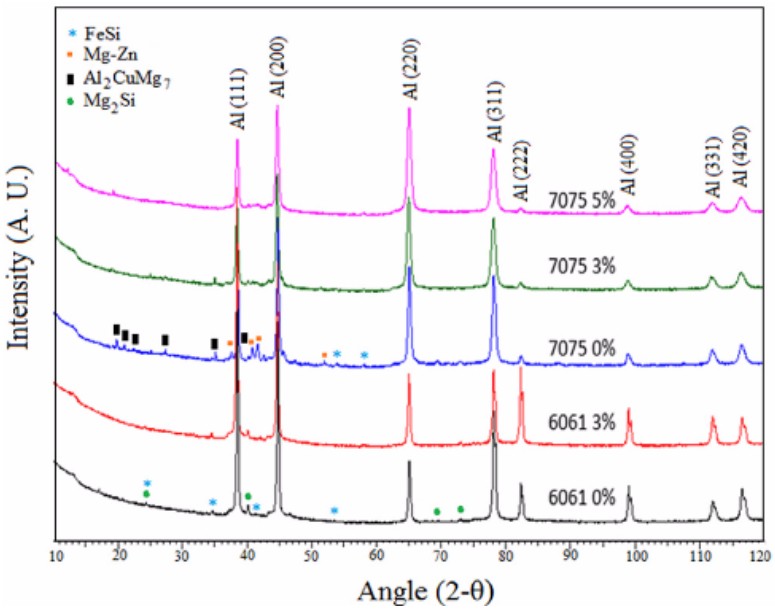

Figure 1. Phase Identification by XRD

What was most interesting from these results was the lattice constant was decreasing as more carbon was introduced into the aluminum matrix. This might imply strong bonding between the Al and C. TEM was used to identify what type of carbon structure was being formed in the material. Folded, ribbon-like structure, similar to graphene nanoribbons and nanosheets were observed in AL-6061 cv 3%. I was not able to perform the experiment myself or interpret the data as I am not a spectroscopy expert, however it was exciting to see the experiment done and the results obtained.

Discussion & Conclusion

The TEM images obtained from Al covetic samples show small regions with higher concentrations of carbon that form arrays of ribbons along directions of the preferred crystallographic directions of the Al lattice starting at the interface between the carbon atom and the Al grain. It is believed that when a current is applied when creating the covetic material, the

carbon atoms become ionized and bond to each other forming chains and layers of carbon which upon solidification of the aluminum around them get trapped along the preferential direction of the Al lattice. We believe the structure is very stable given they maintain that structure after remelting and resolidification. The XRD data showed a surprising result that the lattice constant of the Al matrix actually decreases when the carbon is added possible implying very strong bonding in a sp2 hybridized fashion, which was not normally predicted with standard phase diagrams between carbon and aluminum. Theoretical calculations using DFT can be used to better understand this phenomenon. The covetic materials that we have studied to date have yielded some surprising properties and phenomena not seen in conventional metals: increased electrical and thermal conductivity in metals that are already highly conductive, anisotropic thermophysical properties, and a phase that defies conventional extractive metallurgy refining techniques and whose density appears to challenge the rule in the mixture (as discovered in earlier research). These findings show potential for the utilization of these alloys in high strength and electrical conductivity related applications and also demand further investigation of the phase diagrams of insoluble elements at non-equilibrium conditions for novel functionalized alloys unknown today. There is considerable need for further investigation—of both the structure, and of the physics behind the phenomena we have reported.