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Advances in Nanocarbon Metals: Process

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14. ABSTRACT The addition of nanoscale carbon (C) to a variety of metals was developed by Third Millennium Metals and this class of materials has been called covetics. These materials have several unusual mechanical and physical properties, with potential benefits in improved energy efficiency and material performance over a broad range of applications. During this project, a laboratory scale covetic production system was designed and built. This system addressed the 3 distinct reaction steps: 1) C dissolves in copper (Cu), where the temperature is locally higher, 2) supersaturated C precipitates out on the surface of the liquid Cu as graphene sheets, where the temperature is lower, and 3) stirring disperses the graphene sheets into the Cu. The precipitation of C was demonstrated and shown by scanning electron microscopy and Raman spectroscopy using an arc melter instead of a high-temperature microscope. The main outcome was that the maximum feasible C content in covetics is the C solubility in the metal at the temperature of the arc hot-spot; this maximum is approximately 200 parts per million by mass.					
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Contents

Acknowledgments	iv
1. Introduction	1
2. Conclusions	3
Appendix. Covetics	5
Distribution List	18

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1. Introduction

A new process technology provides the ability to add greater than 6-wt% nanoscale carbon (C) to a broad variety of metals. The resulting materials, developed by Third Millennium Metals, LLC, are known as “covetic” nanomaterials.¹ These materials have several unusual properties, notably increased strength, increased thermal conductivity, and increased electrical conductivity, with potential benefits in improved energy efficiency and material performance over a broad range of applications and industries including defense.

This examination of covetics is part of a Defense Advanced Research Projects Agency–funded program involving the University of Maryland (UMD), Carnegie Mellon University (CMU), and the Naval Surface Warfare Center, Carderock Division. The proposed project at CMU specifically deals with copper (Cu)-based covetics (see Appendix). The procedure used to produce the material has been described in the patent from Third Millennium Metals. The essential elements of the process are: 1) a C source is brought into contact with molten Cu, 2) current is applied to the Cu by means of C electrodes, and 3) mechanical stirring is applied simultaneously. Through this combination of steps, what appears to be nanosized C is produced and dispersed into the molten Cu. The overall process is endothermic, where a drop in the temperature of the melt is witnessed when current is applied.

The problem addressed in this research is that the fundamental steps that lead to the formation of covetics are not known; the patent¹ contains the following:

While the exact chemical structure of the disclosed metal-carbon material is currently not known, without being limited to any particular theory, it is currently believed that the steps of mixing and applying electrical energy result in the formation of chemical bonds between the metal and carbon atoms, thereby rendering the disclosed metal-carbon compositions unique vis-a-vis known metal-carbon composites and solutions of metal and carbon.... Furthermore, without being limited to any particular theory, it is believed that the disclosed metal-carbon material is a nanocomposite material and ... the amount of electrical energy (e.g., the current) applied to form the disclosed metal-carbon composition initiates an endothermic chemical reaction.

This creates a difficult problem. While the practical steps required to produce covetics have been described by the inventors, there is no information on the fundamental mechanism of covetic formation. In further refining the process, the

current approach by the developer of the technology (Third Millennium Metals) is to rely on empirical knowledge. An obvious limitation to this empirical approach is that there is little or no quantitative basis for scaling-up or optimizing the process.

The current project proposes that the process can be separated into 3 distinct reaction steps. If this is indeed the case, each of these steps can be executed in a separate reactor. Such separation of process steps would allow tighter control of process conditions and allow the process to be converted readily to continuous production (rather than the current batch process).

The essential technical idea is captured in the following hypotheses:

- Covetic consists of graphene sheets distributed within the metal (Cu).
- The applied current causes local heating where the electrodes enter the Cu melt.
- C dissolves in Cu where the temperature is locally higher (Step 1).
 - Where the temperature is lower, supersaturated C precipitates out on the surface of the liquid Cu as graphene sheets (Step 2).
- The role of stirring is to disperse the graphene sheets into the Cu (Step 3).
 - The observed endothermicity results from the small exothermic bonding energy between liquid Cu and graphene, which is much smaller than the energy involved in breaking Cu-Cu bonds when dispersing graphene in the Cu.
 - Previous combustion analysis failed to detect C in Cu covetic material because the oxidation rate of the covetic material is significantly lower than that of pure Cu.

The proposed scope and deliverables of the program are described in the following 6 procedural tasks:

- 1) Design and build a laboratory-scale system for Cu covetic production. Also, produce additional samples of covetic Cu, to be analyzed by the team at the UMD.
- 2) Theoretical evaluation of the energy balance of the process.
- 3) Experimental measurement of the oxidation rate of molten Cu and molten covetic Cu in pure oxygen (O).

- 4) Experimental test, using a high-temperature microscope (laser scanning confocal microscopy), of the proposal that C dissolves from the C source at higher temperature and precipitates as graphene upon cooling.
- 5) Experimental test, using the laboratory-scale covetic process, of the extent of local heating caused by the applied current to determine whether the local heating is sufficient to sustain C dissolution (as a necessary step before C precipitation as graphene).
- 6) Preparation of an overall summary report, stating the process implications of the fundamental information obtained in this project.

2. Conclusions

This project was successful in completing all of the tasks contained within the proposal scope. While not all of the research organizations came to the exact conclusions, a significant amount of data was created that can be interpreted for any future covetics research. The new laboratory-scale covetic production facility at CMU could be an instrumental part of a potential larger program.

The following outcomes were achieved for the proposed program tasks:

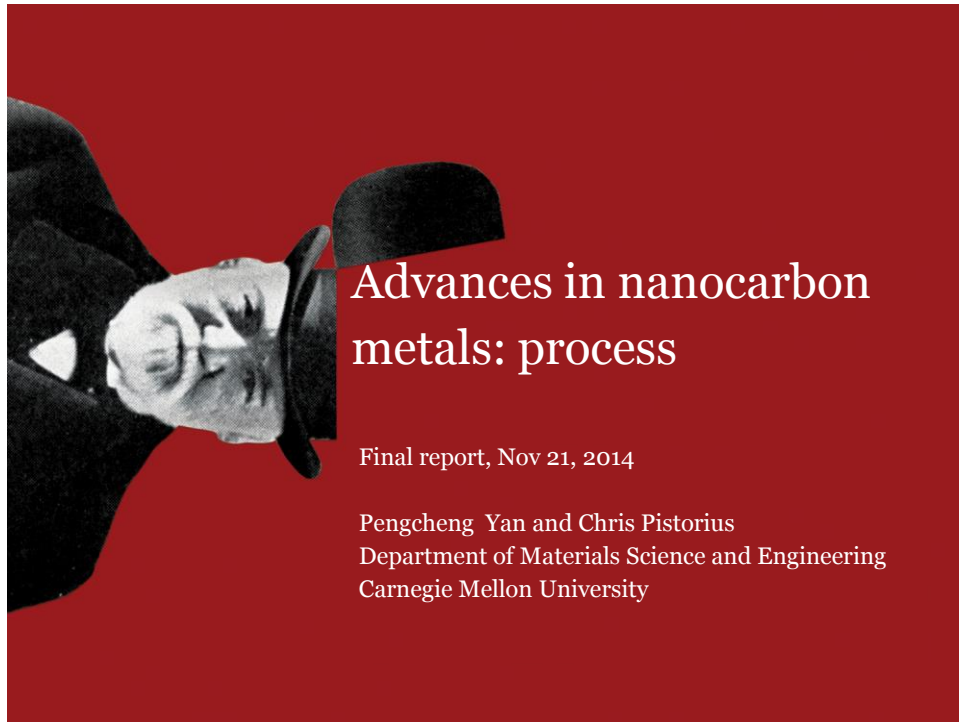
- 1) Completed the design and build of a laboratory-scale system for covetic production. Cu and silver (Ag) covetic samples were produced for UMD analysis.
- 2) Completed the theoretical evaluation of the energy balance of the process. This assessed the creation of Cu-C interfaces as a possible cause of the endothermic effect reported by Third Millennium. However, given the small concentration of C actually produced, this effect is negligible.
- 3) The experimental measurement of the oxidation rate of molten Cu and molten covetic Cu in pure O was completed. No difference in oxidation behavior was seen. Testing of C concentration in Cu and Ag was developed via full oxidation in O (with infrared analysis of off-gas). Material produced by Third Millennium was tested and found to contain less than 50 parts per million (by mass) of C in all cases.
- 4) Demonstrated precipitation of C shown by scanning electron microscopy and Raman spectroscopy using an arc melter instead of a high-temperature microscope.
- 5) Completed the measurement of the local heating caused by the applied current using the laboratory-scale covetic process. Using an infrared

camera, the local hot-spot temperature (beneath the arc) was measured as approximately 2,000 °C.

- 6) In addition to this report, a draft paper on the project results has been written and will be submitted for journal publication. A copy of that submission will be supplied as soon as it is sent to the journal. The processing knowledge collected during this work is summarized in a kinetic model. The main outcome is that the maximum feasible C content in covetics is the C solubility in the metal at the temperature of the arc hot-spot; this maximum is approximately 200 parts per million by mass.

Appendix. Covetics

This appendix appears in its original form, without editorial change.



Content

Focus of project: produce covetics

- Covetics
 - Challenges
 - Process mechanism
- Experimental & results
 - Small scale arc melting
 - Covetics production
- Kinetics model
- Summary

Covetics

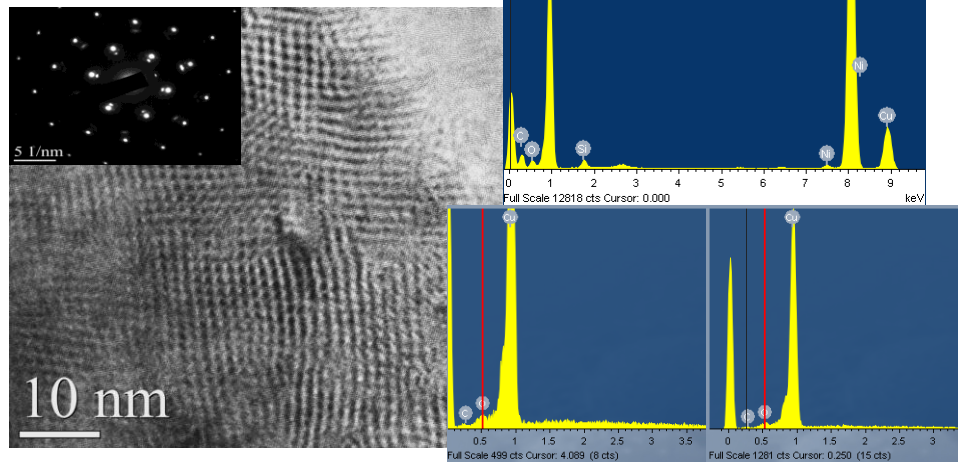
- Metal – nanocarbon composite
 - Au, Ag, Cu, Zn, Al etc
 - “Single phase”
 - Upto 6 wt % carbon
- Improved properties
 - Thermal/electrical conductivity
 - Strength
 - Density

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Challenge

- Carbon content



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4

Challenge

- Carbon content by
 - EDS, XPS, SIMS (microanalysis)
 - LECO (0.5 gram, fast combustion), **full slow oxidation**

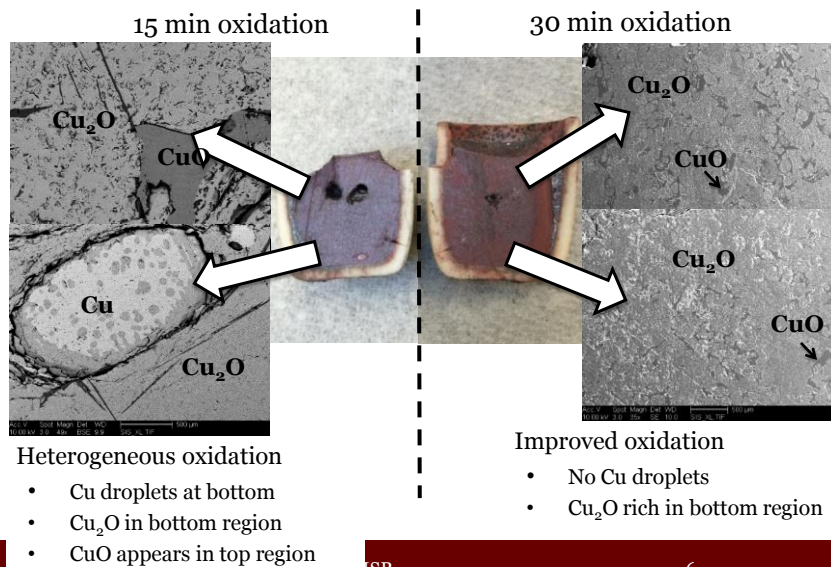


1. Pre-heating: Al_2O_3 crucible in O_2 at 1200 °C for 2 hour
2. Calibration
 - pure Cu oxidised for 30 mins (background)
 - known graphite in Cu tube ($\Delta \sim 0.5\%$)
3. Measurement: oxidation at 1200 °C for 30 mins

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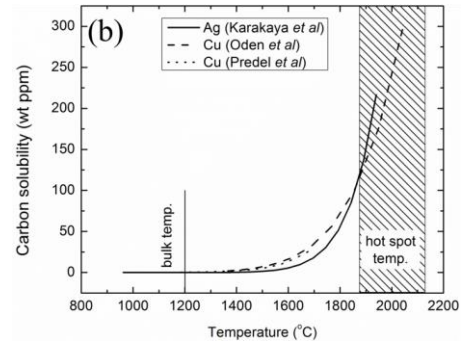
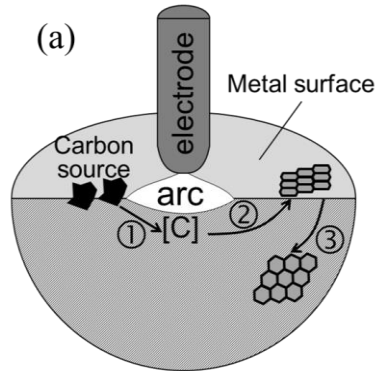
Full oxidation



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6

Process mechanism

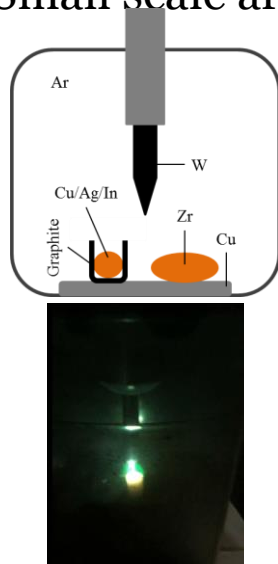


1. Carbon source dissolves in liquid copper at hot spot beneath arc.
2. Copper flows away from arc; dissolved carbon precipitates as nano-carbon at the free surface of the melt.
3. Mechanical stirring distributes nano-carbon through the melt.

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7

Small scale arc melting



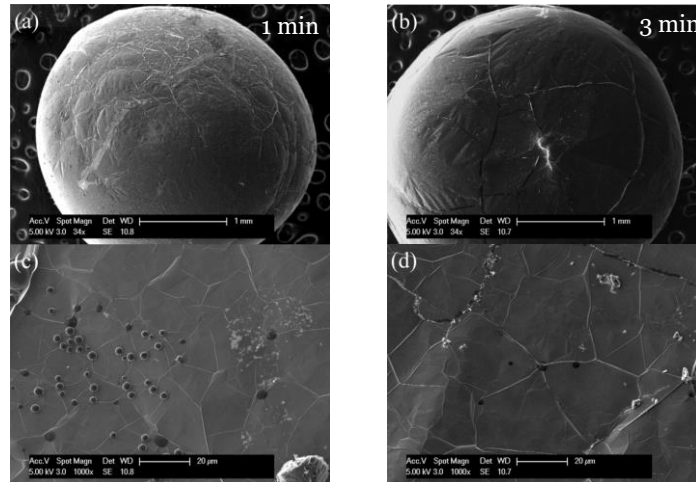
- Arc-melt Cu/Ag under purified argon
 - in high-purity graphite crucibles, for different times
 - to test steps ① and ②

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Small scale arc melting

- Carbon on Cu surface

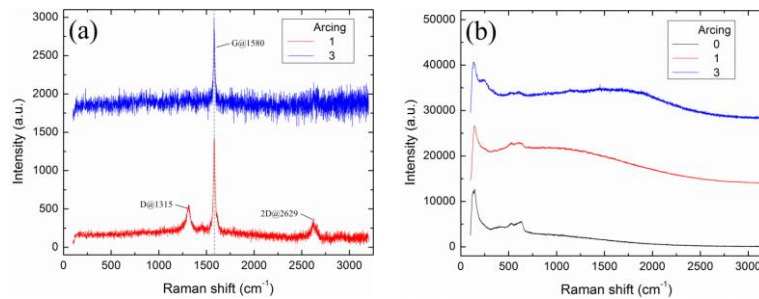


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Small scale arc melting

- Carbon on & in Cu



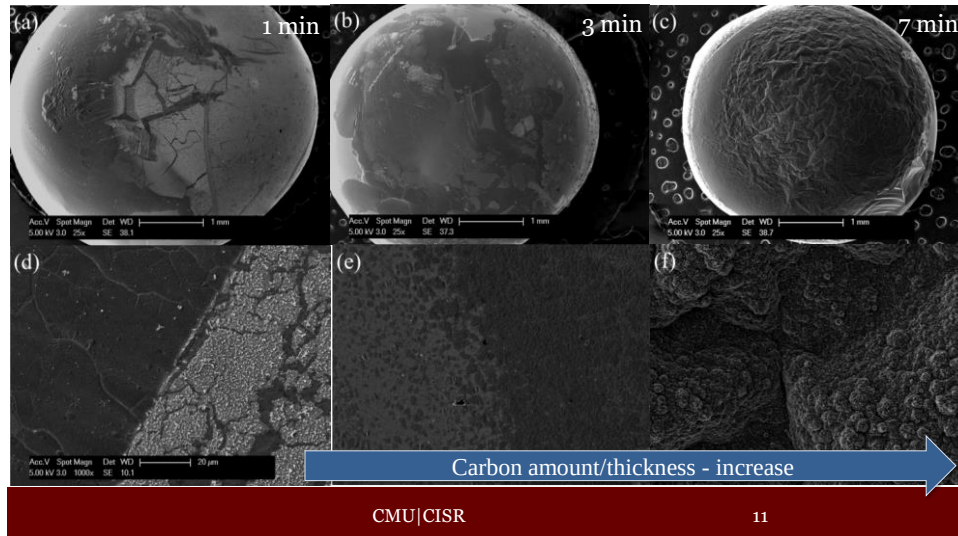
- C film on Cu surface
 - Thickness increases with arcing duration
 - sp² carbon
- Broad peak in bulk: amorphous carbon
- Steps ① and ② confirmed for Cu

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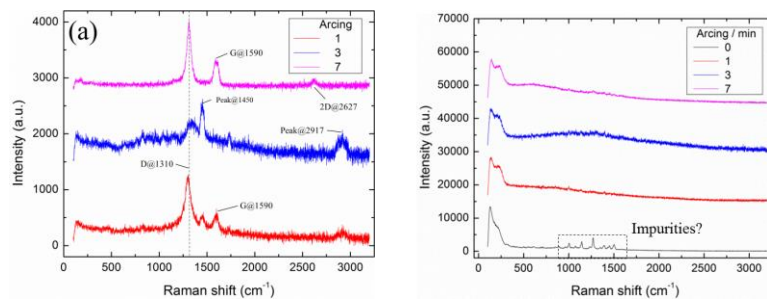
Small scale arc melting

- Carbon on Ag



Small scale arc melting

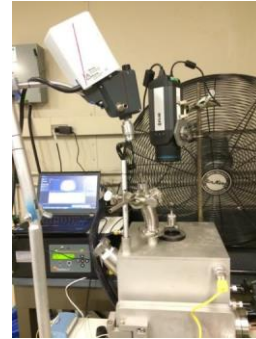
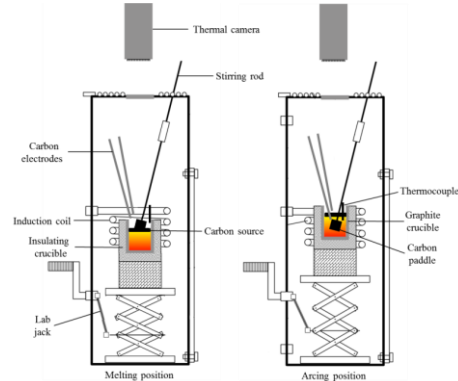
- Carbon on & in Ag



- C film/particles on Ag surface
 - Thickness increases with arcing duration
 - sp² carbon
- No or limited carbon in bulk
- Steps ① and ② confirmed for Ag

Covetics production

- Set-up

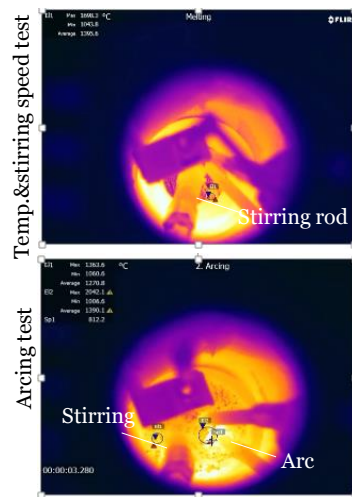


- One electrode in melt; another one just above carbon source
- Temperature: thermocouple-before arcing; thermal camera-during arcing

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13

Covetics production



- Melting
 - Solid Cu $\epsilon=0.2$
 - Molten Cu $\epsilon=0.06$
- Stirring
 - $\epsilon=0.2$
 - Temp. vibration
 - ~ 150 rpm
 - ~ 23 mm/s @ $r=1.8$ cm
 - ~ 35 mm/s @ $r=2.7$ cm
- Arcing
 - $\epsilon=0.2$
 - Large Temp. increase

ϵ : emissivity; observation window becomes dirty, leading to low ϵ

* If need the original videos, please contact CMU

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14

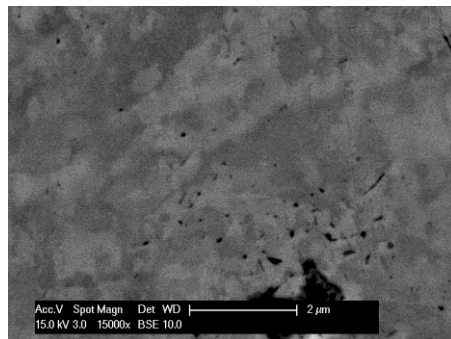
Covetics production

Sample	Remarks	Stirring / min	Arcing / s	Graphite / wt%	Activated Carbon wt%	Measured Carbon	
						IR	LECO
0	Cu	0	0	0	-	0	12
1		5	0	5	-	0	12
2		5	78	5	-	9	14
3		5	32	0	-	1.5	
4		30	237	5	-	48.5	17
5		10-5	60	0.003	-	40	
6		10-5	300	5	-	33	
7		15-5	360	-	2.5	107	
8		15-5	180	-	2.5	30	
9		10-5	0	-	2.5	6	
10		10-5	240	-	2.5	32	
11		10-5	60	-	0.5	29.5	
12		10-5	120	-	0.5	45	
13		10-5	180	-	0.5	51.5	
14		10-5	150	-	0.5	63	
15		-5	600	-	0.5	99	
16		-5	600	-	0.5	102.5	
17		-5	1020	-	0.5	70	
18		-5	1020	-	0.5	40.5	
19		-5	1410	-	0.5	134.5	
20		-5	90	-	0.5	40	
1	Ag	-5	300	-	0.5	73	

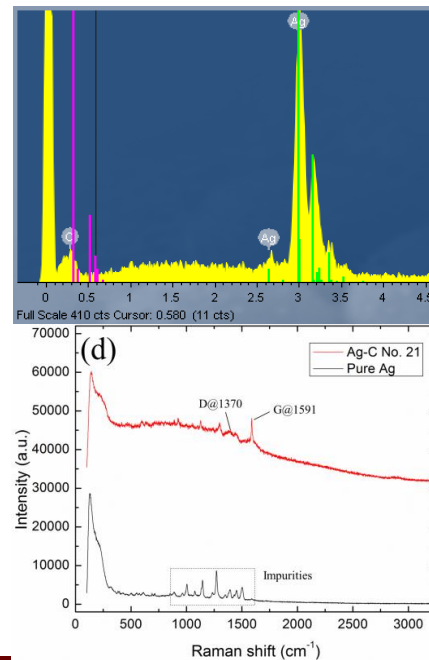
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15

Ag covetic



- Nano particle or pores
- Carbon peak
- D and G peaks, sp^2 carbon
- Steps ③ confirmed for Ag

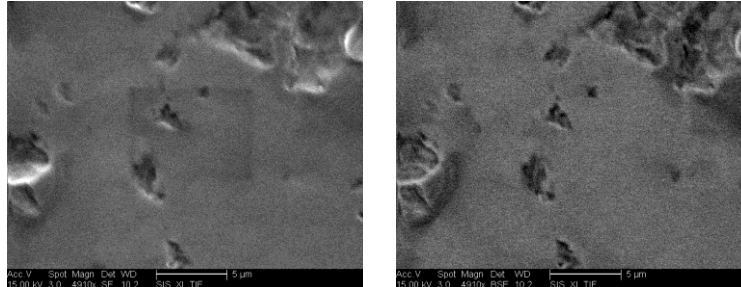


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16

Cu covetic

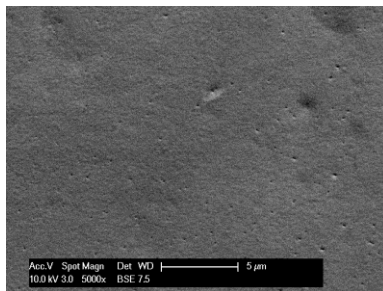
- Short arcing samples



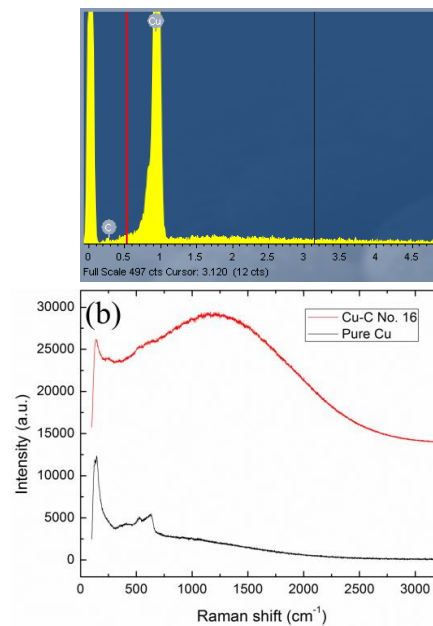
- No Carbon in covetic samples (short time arcing)

Cu covetic

- long arcing samples

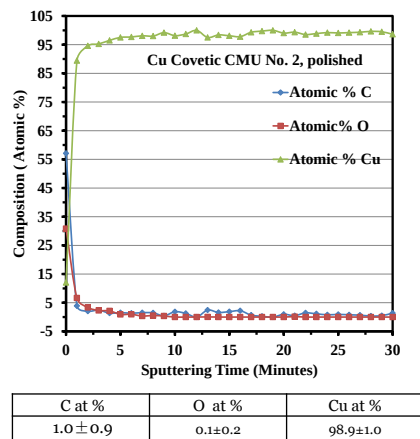


- Nano pores on polished samples
 - Small carbon peak with EDS
 - Broad peak, amorphous carbon?
 - Steps ③ confirmed for Cu



Carbon content

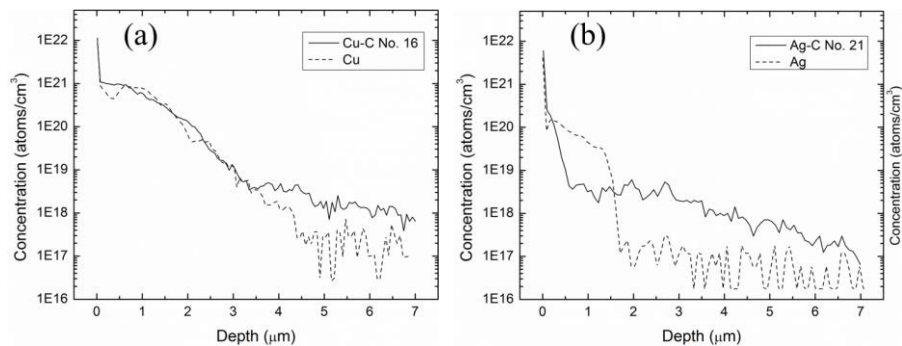
- With XPS



- Carbon on surface not in bulk

Carbon content

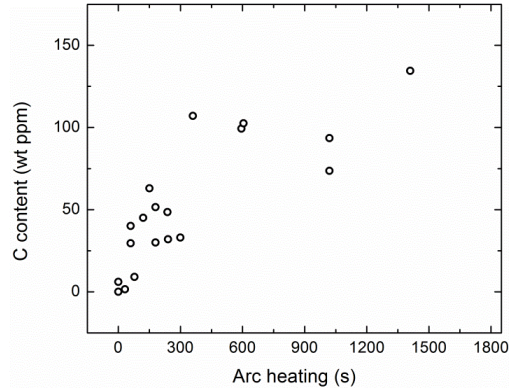
- With SIMS



- Higher carbon in covetics than raw materials
- Need bulk analysis

Carbon content

- With full oxidation



- Increases with arcing, reaching 150 ppm in mass
- Limiting step?

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21

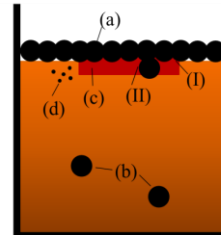
Kinetics model

- Assumption

- Limited by carbon dissolution in hot spot
 - Hot spot size
 - Stirring speed/flow rate
 - Temperature

$$(I) \quad \frac{dC'}{dt} = \frac{kA}{V'} (C_s - C')$$

$$(II) \quad \frac{dC_s}{dC'} = (1 - \frac{r}{\tau})^{1/2}, \quad \tau = \frac{\rho_C (d_o^2)}{8D_C (C_s - C')}$$



- Constant volume, density ($\rho_{C, Cu}$) and initial C particles diameter (d_o)
- Nano-carbon homogeneously dispersed in Cu bulk

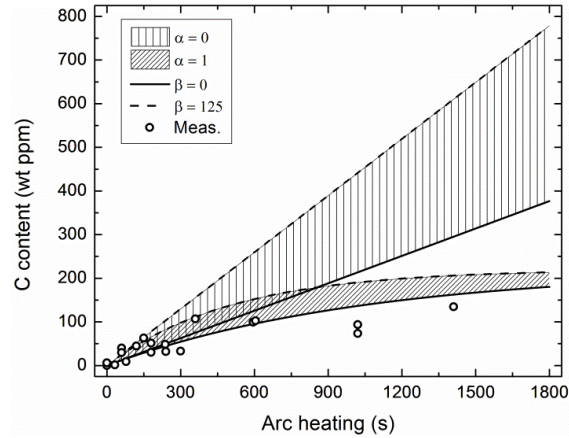
- Conditions

- Precipitated nano-carbon particles redissolution
 - $C_t^0 = \alpha C_t^{\infty}, \alpha = 0-1$

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Kinetics model



Parameters:

- $k=7\text{e-}4$ m/s
 - $Re=32632$
 - $Sc=0.22$
 - $D_C=5.2\text{e-}7$ (D_O @ 2000 °C)
 - $k=\sim 2\text{-}3\text{e-}4$ m/s in liquid Fe @ 1550 °C
- $C_s=220$ ppm @ 2000 °C
- $A_h=1\text{e-}4$ m²
- $h=2\text{e-}4$ m
- $V_h=2\text{e-}8$ m³
- $d^o=1\text{e-}3$ m
- $\Delta t=0.1$ s

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