Feasibility Studies of Cyanide-Free Gold Plating Solutions For Electronic Connector Plating Applications

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Feasibility Studies of Non-CN Hard Au

Abstract

Increasingly stringent regulatory restrictions on the chemical industry continue on a global basis. Governmental regulations may in some cases force manufacturers to abandon well-established, proven solutions and force the adoption of inferior, non-feasible and/or higher cost solutions in order to be in compliance. A recent example is a policy statement issued by China's "National Development and Reform Commission" (NDRC) in March 2013, of which a summary translation states: "Any plating process containing toxic and hazardous cyanide (i.e., gold plating of potassium gold(III) cyanide (KAu(CN)4) and potassium aurocyanide (KAu(CN)2)) will be banned by the end of 2014". This regulation was met with widespread industry resistance and in September 2013 the government decided to postpone the legislation. However, most users of potassium gold cyanide (PGC) consider this to be a warning and it is expected that the legislation will ultimately be enacted. The electronic plating industry is the largest user of PGC in China and globally. While it is technically feasible to replace PGC in some applications - particularly those involving pure gold in rack or barrel plating applications - so far no process has been developed that is free of PGC in high speed 'hard' alloyed gold applications which are most commonly used in the electronic connector plating industry.

This paper will describe the challenges involved in formulating a plating process chemistry which is free of all cyanide-compounds (including PGC) for electronic connector plating applications. Studies of several different electrolytes will be presented, and a novel solution will be introduced which satisfies the basic properties required as a contact finish for the connector plating industry.

Feasibility Studies of Non-CN Hard Au Introduction

- Potassium Tetracyanoaurate ($KAu(CN)_4$) commonly known as potassium gold cyanide or PGC, is the main source of gold metal used in the electroplating industry today
- Global regulatory environment is increasingly challenging for plating chemistry applications
  - In some regions, use of cyanide-containing compounds may be severely restricted / outright banned

Proposed Ban on PGC in China

- On March 20, 2013, a statement was issued by the “National Development and Reform Commission” (NDRC) of China which stated:
  - “Any plating process containing toxic and hazardous cyanide (gold plating of potassium gold(III) cyanide (KAu(CN)4) and potassium aurocyanide (KAu(CN)2) will be banned by end-2014 and it will be replaced by alternatives which are recommended from the list of “State encouraged recyclable technology and equipment”
- This started a global frenzy of activity focused on present usage and possible replacement of PGC
- Six months later, on September 23, 2013, the NDRC announced the proposed legislation was being postponed
- Despite the postponement of the legislation, many companies consider this a ‘warning’ and expect that PGC will ultimately be banned in China once a viable alternative is found.

Newspaper Article in “Oriental News”, Hong Kong, April 25, 2013:

2013.04.25 星期四

東方日報

專題新聞 A 8

發改委全國推介 港商大手入貨中招

無毒電鍍產品

驗出劇量山埃

江門警方化驗報告顯示，丙爾金（圖）含有氰化金鉀及檸檬酸鉀。

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CN-free Gold Plating

- Gold plating chemistry which is truly cyanide-free is possible using a gold sulfite electrolyte
  - Sulfite gold plating chemistry is well-known and established since the 1950s
- However, gold sulfite solutions have traditionally been used only for pure (soft) Au plating in rack and barrel applications
  - Not suitable for hard Au ‘high speed’ / reel-to-reel connector plating
- Significant challenge exists to produce a hard Au deposit from a non-cyanide electrolyte, that fulfills the requirements of high speed / reel-to-reel connector plating applications

Non-CN Hard Au Process Evaluations Introduction

- Non-CN Au processes were formulated and evaluated for use in connector plating and compared to conventional PGC-based hard Au systems for:
  - Hardness
  - Contact resistance
  - Wear resistance
  - Corrosion resistance

Non-CN Hard Au Process Evaluations Test Methodology

- Hardness:
  - Knoop hardness indenter
- Contact Resistance
  - Per ASTM B667-97 / ASTM B539-02
  - Output: resistance vs. normal force
    using 4 pt. probe with 10-300g load normal force

  →Acceptance Criteria: C.R. < 10 m-ohms / stable
- Wear Resistance
  - Per ASTM G-133-05
  - Output: Coefficient of Friction (CoF) vs. # of cycles
    using 200 g load; 0-50 cycles

  →Acceptance Criteria: CoF < 0.8 after 50 cycles
  - Wear Track analysis (SEM)

Non-CN Hard Au Process Evaluations Test Methodology (cont.)

- Corrosion Resistance

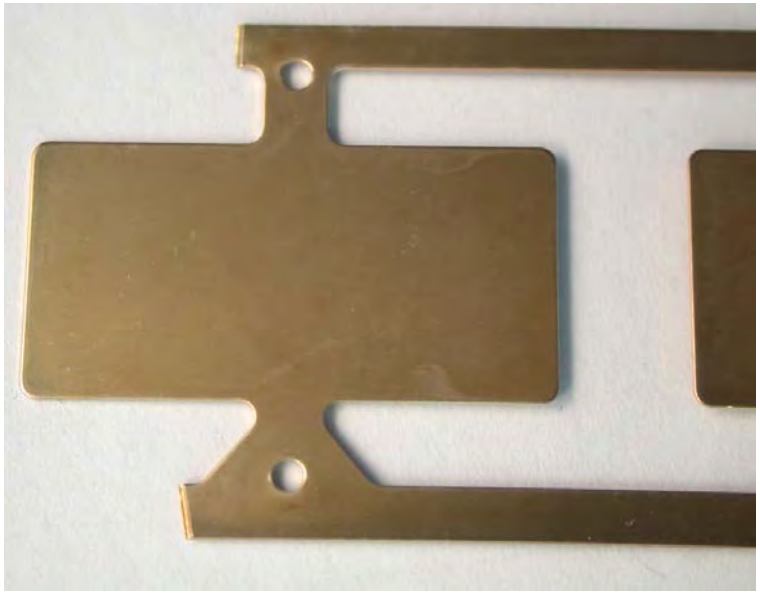
  Visual deposit appearance evaluation after exposure to corrosive environment

  (I) NAV Testing: per ASTM B735-05. 2 hour exposure

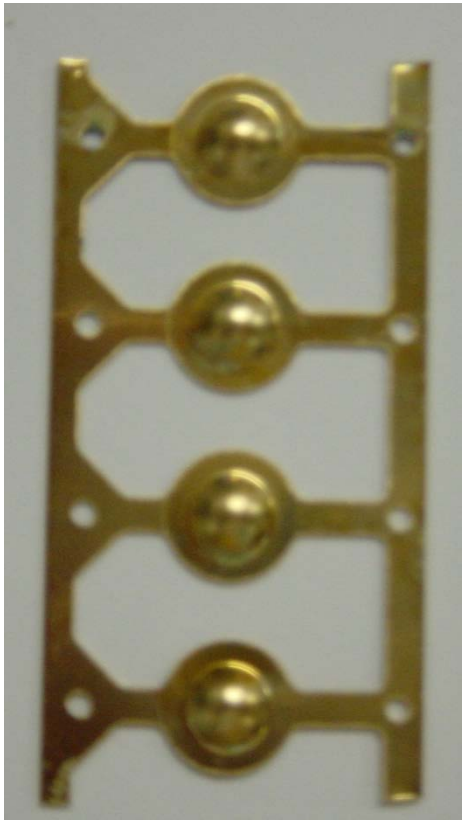
  (II) MFG: per EIA-364-65B; Class IIa; 5 days exposure

  →Acceptance Criteria: no pores/corrosion products in critical contact area. CR checked after MFG exposure.

Non-CN Hard Au Process Evaluations Test Vehicles

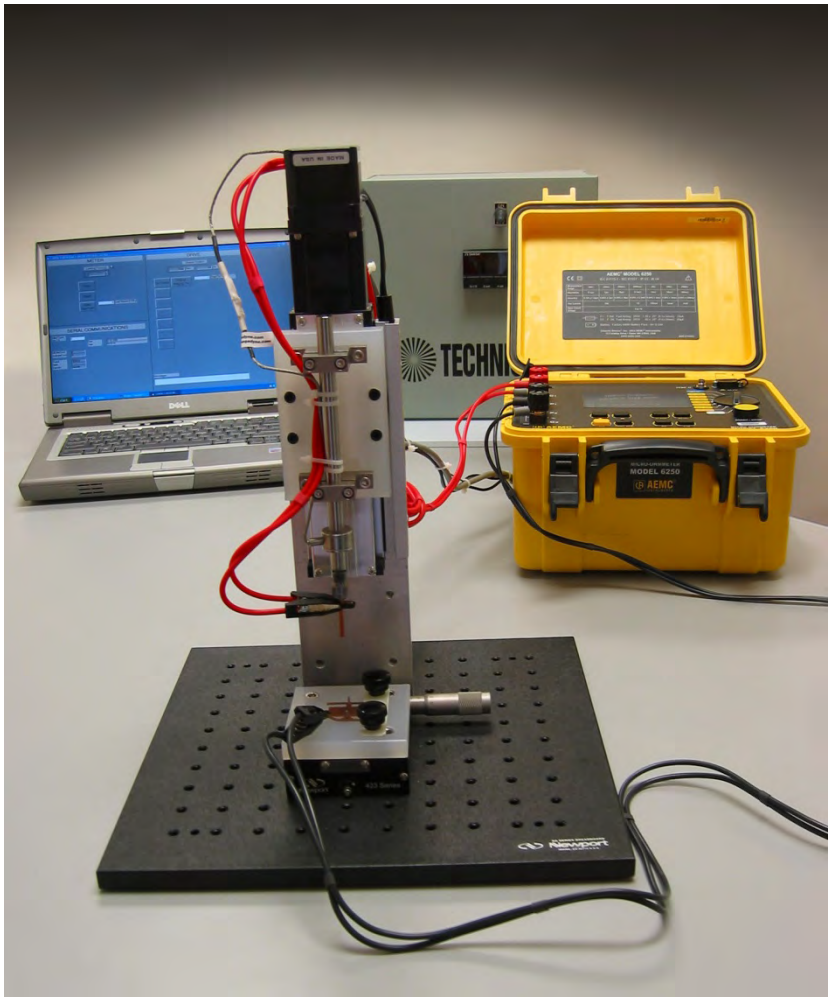


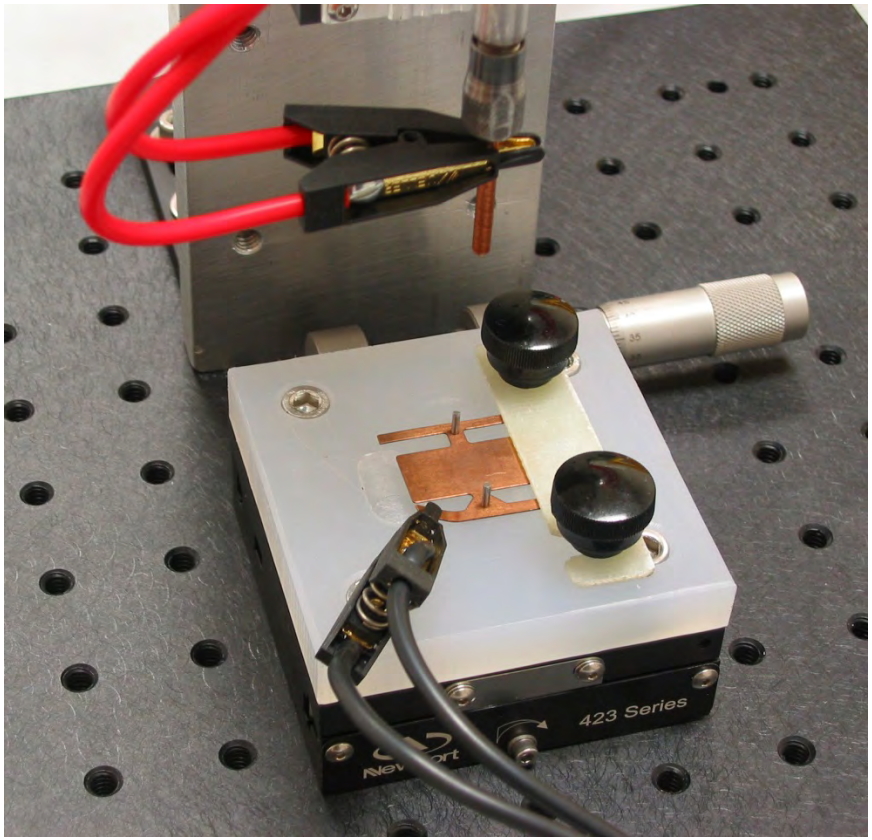
Plaque



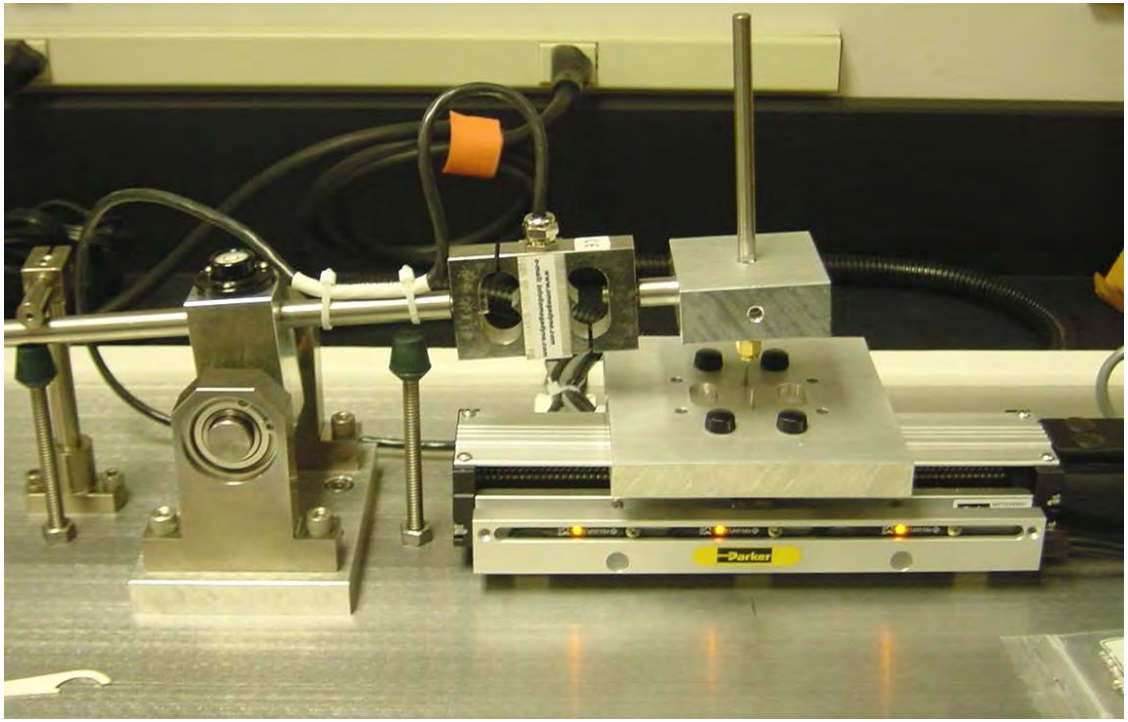
Probe

Contact Resistance Test Equipment

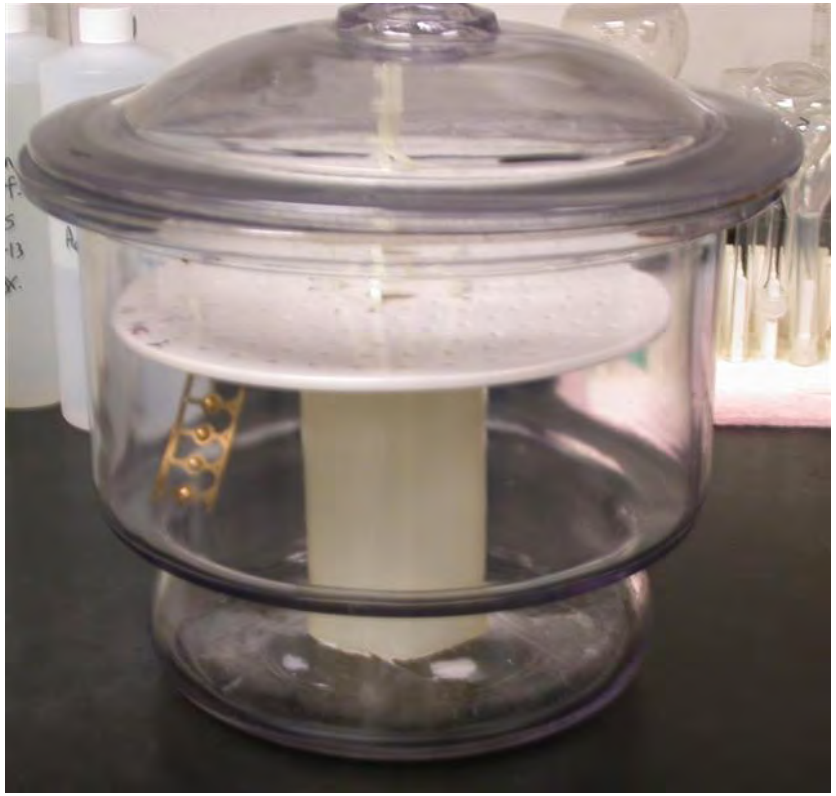




Wear Resistance Test Equipment



Corrosion Resistance (I)
NAV Test Equipment



Corrosion Resistance (II) Mixed Flowing Gas (MFG) Test Conditions

- MFG Tests are performed by an independent, certified lab, following the conditions of EIA-364-65B, Class IIa.

Temperature = 30°C +/- 1°

Relative Humidity = 70% +/- 2%

Cl_2 = 10 +/- 3 ppb

$N0_2$ = 200 +/- 50 ppb

H_2S = 10 +/- 5 ppb

SO_2 = 100 +/- 20 ppb

Test Duration = 5 Days

Non-CN Hard Au Process Evaluations
Solution Makeup Conditions

Process #1: Control (PGC):

Component	Quantity
Electrolyte Salts	150 g/l
Au metal as PGC	8 g/l
Ni metal	900 ppm
Range Extender (additive)	15 ml/l
pH	4.5
Temperature	55°C

Process #2: Non-Cyanide (Rev. I) :

Component	Quantity
Electrolyte Solution	500 ml/l
Au metal as Gold Sulfite	8 g/l
Hardening agent (additive)	30 ppm
Stabilizer	5 g/l
pH	7.5
Temperature	55°C

Non-CN Hard Au Process Evaluations
Test Sample Plating Sequence

All samples were processed as follows:

1. Clean / activate
2. Nickel Plating: 2.0 ± 0.5 µm at 10 A/dm^2
3. Au plating: 0.75 ± 0.1 µm at 10 A/dm^2
4. Rinse/Dry

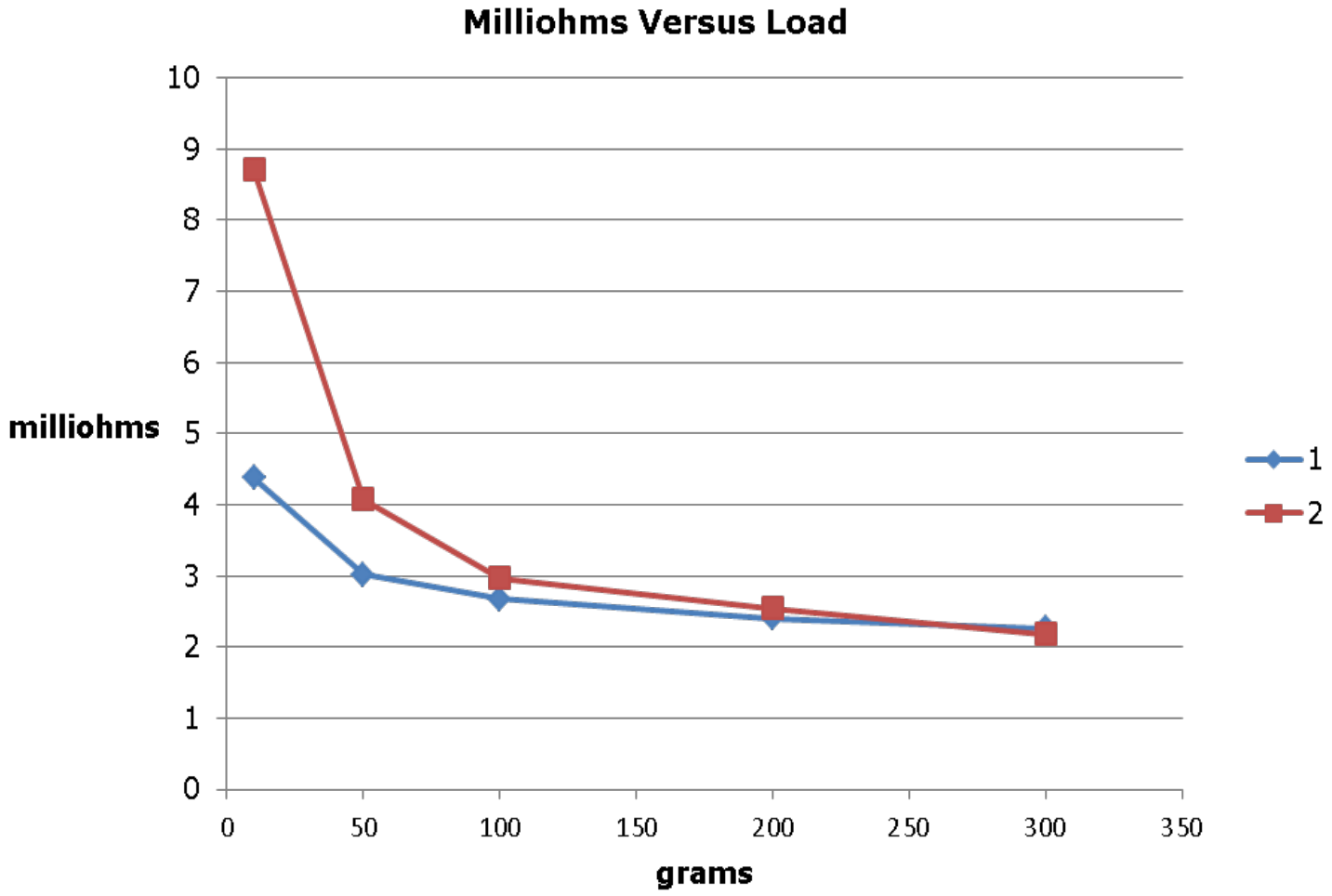
Note: intermediate water rinses omitted for clarity

Plated samples then proceeded to deposit evaluations

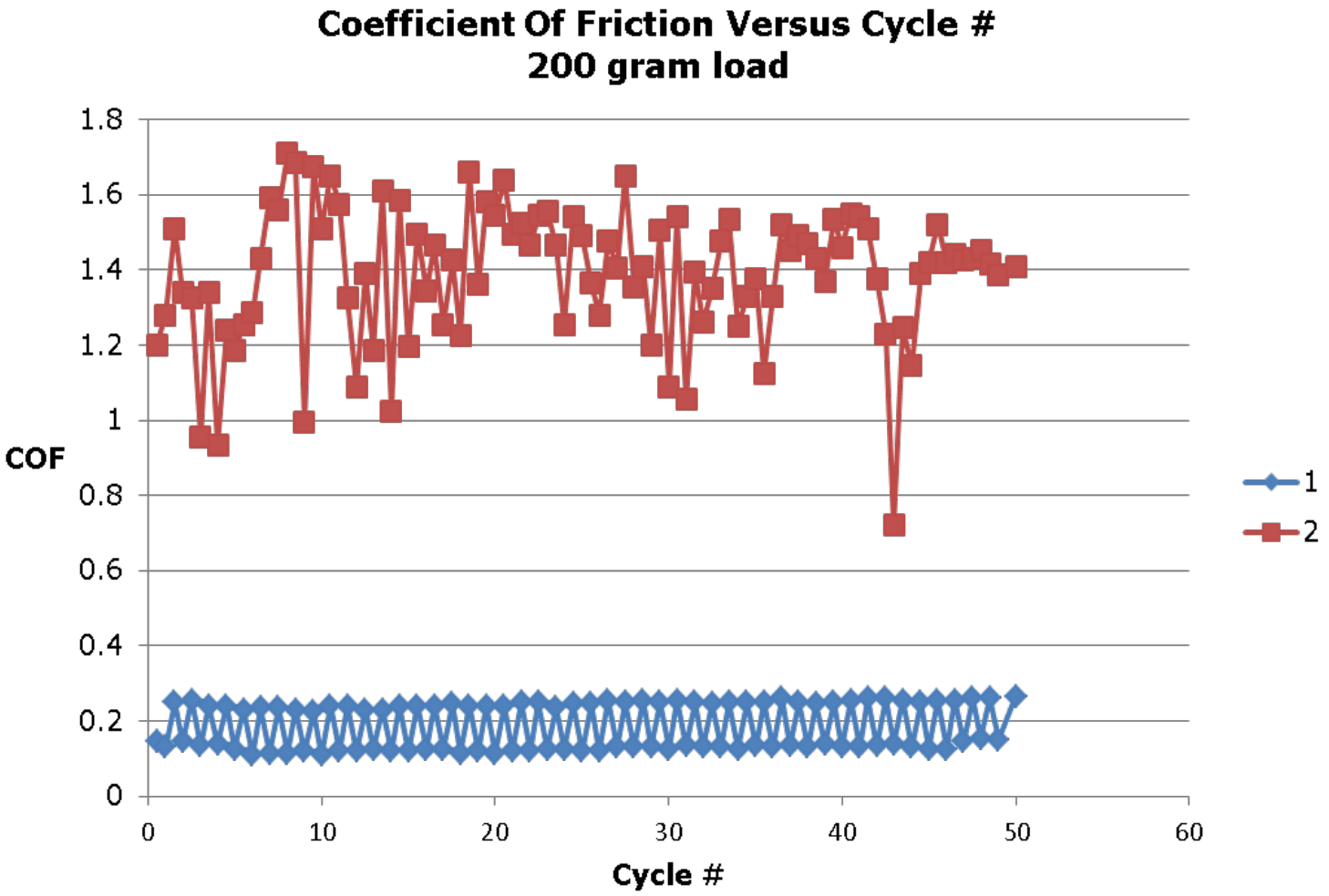
Non-CN Hard Au Process Evaluations
Knoop Hardness

Deposit #1: 130 Knoop
Deposit #2: 125 Knoop

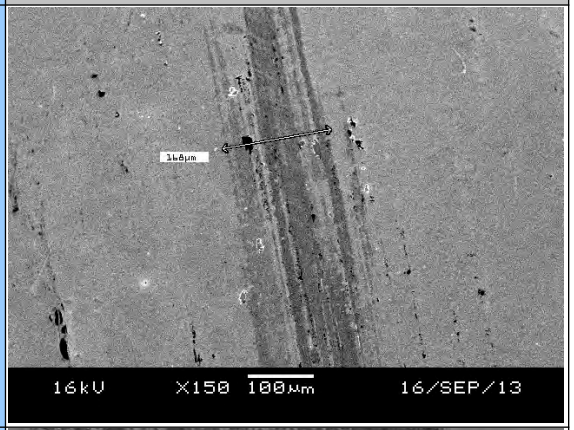
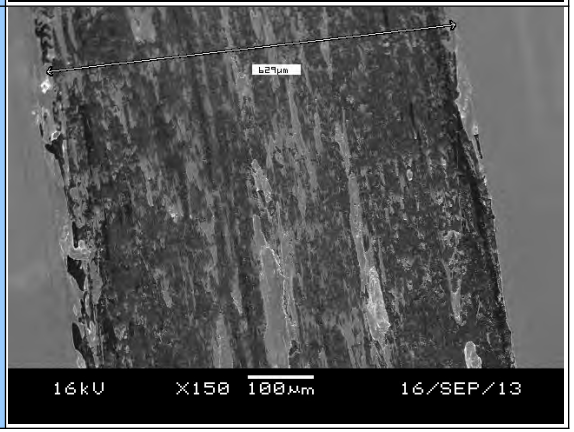
Non-CN Hard Au Process Evaluations Contact Resistance – Processes 1 & 2



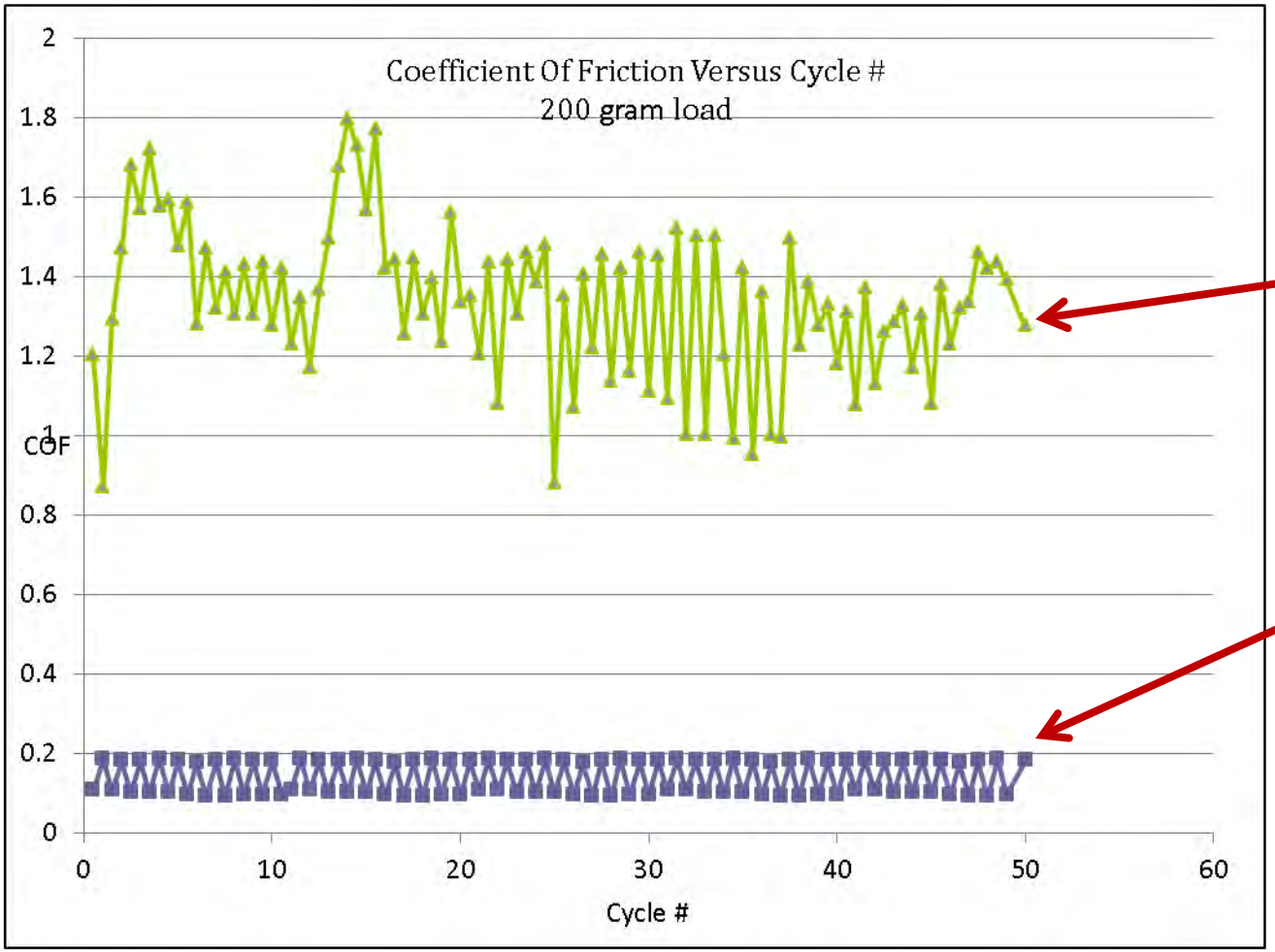
Non-CN Hard Au Process Evaluations Wear Resistance – Processes 1 & 2



Non-CN Hard Au Process Evaluations
Wear Track Analysis – Processes 1& 2

DOE Run #/ Parameters	Track Width (µm)	SEM Photos 150x
Run #1/ 60 µ-in Ni + 30 µ-in Au (PGC)	168	
Run #2/ 60 µ-in Ni + 30 µ-in non-CN Au Rev I	629	

Non-CN Hard Au Process Evaluations
Wear Resistance
Process 2: With and without lubricant



Run #2:
As-plated

Run #2:
With lubricant

Observations
CR, Hardness, & Wear Resistance

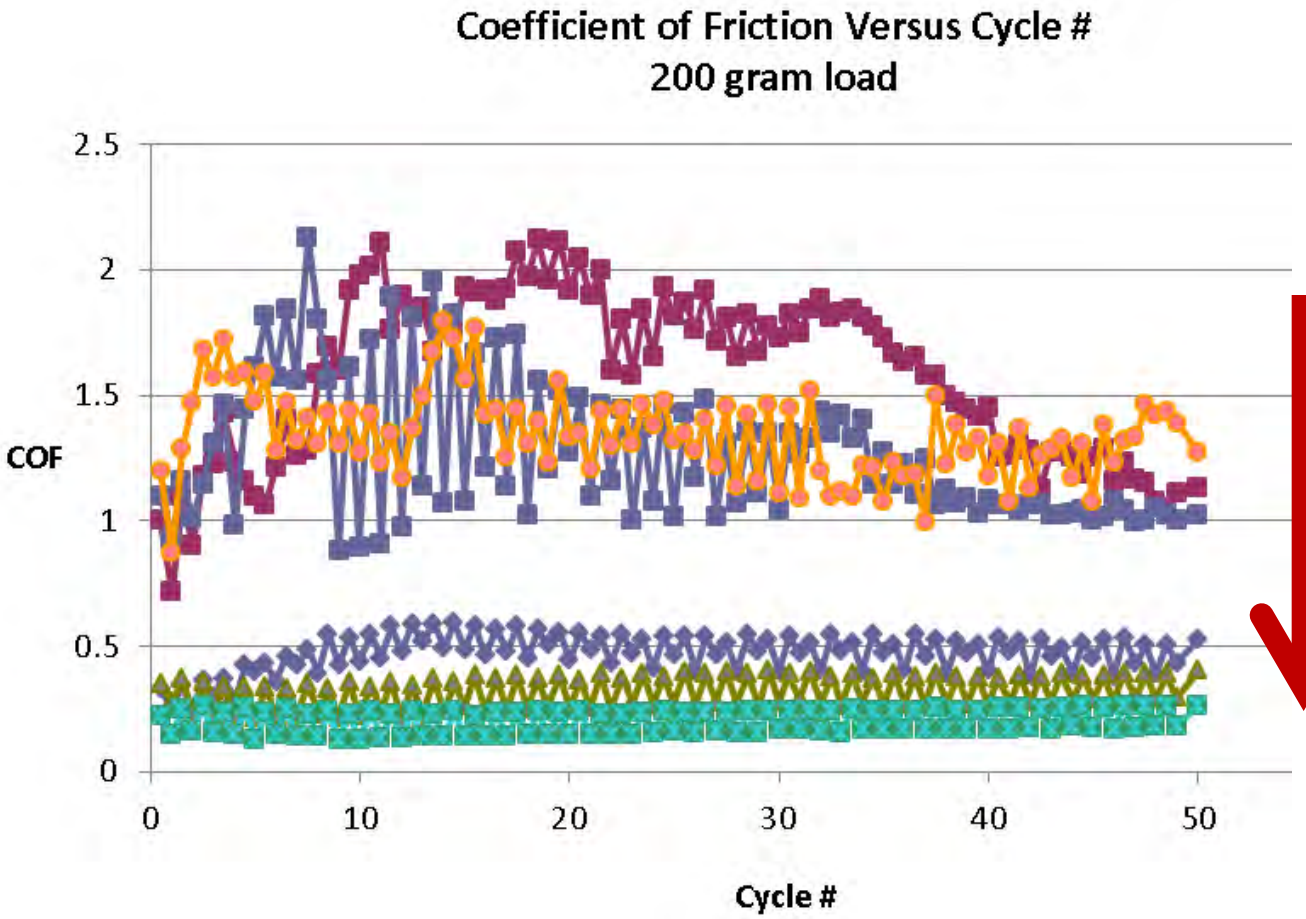
- The contact resistance and hardness of deposits produced from Processes #1 and #2 were similar and typical of hard Au
- However, wear resistance results indicated the PGC Process #1 produces very good WR results while the non-CN Process #2 produces poor WR results.
  - Wear Track analysis results paralleled the CoF results.
  - *High hardness does not necessarily correlate to good wear resistance performance*
- Use of a lubricant provides the expected improvement in wear resistance performance of Process #2, but a more robust solution is needed
- The non-cyanide gold solution was modified with the objective of improving the wear resistance without use of a lubricant

Non-CN Hard Au Process Evaluations Process #3

Process #3: Non-Cyanide (Rev. II) :

Component	Quantity/liter
Electrolyte Solution	650 ml
Stabilizer	5 g
Gold as gold sulfite	8 g//l
Nickel Metal	2000 ppm
pH	4.5
Temperature	55°C

Non-CN Hard Au Process Evaluations
Process #3: Effect of Ni conc. on WR

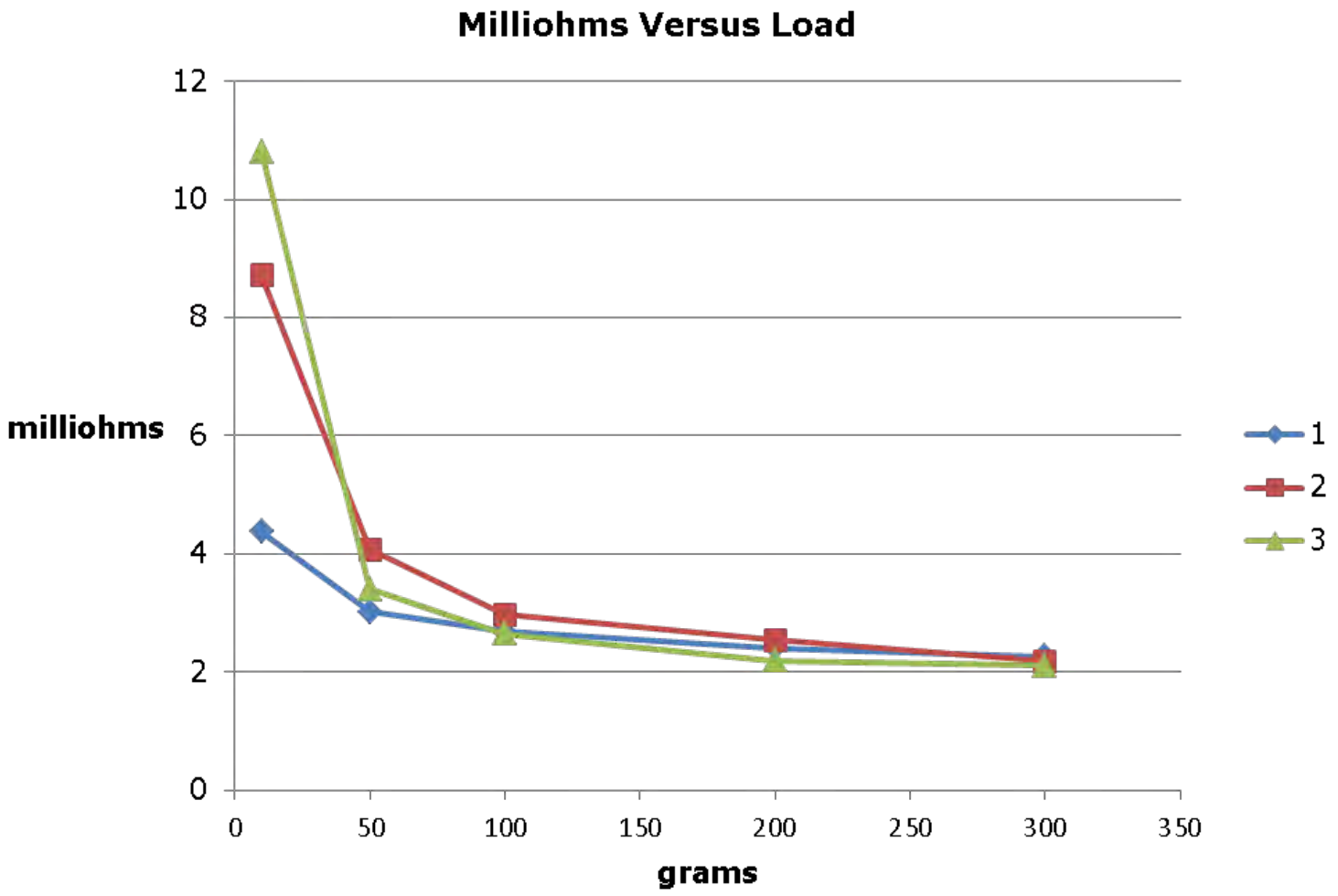


As Ni concentration in solution increases, CoF decreases

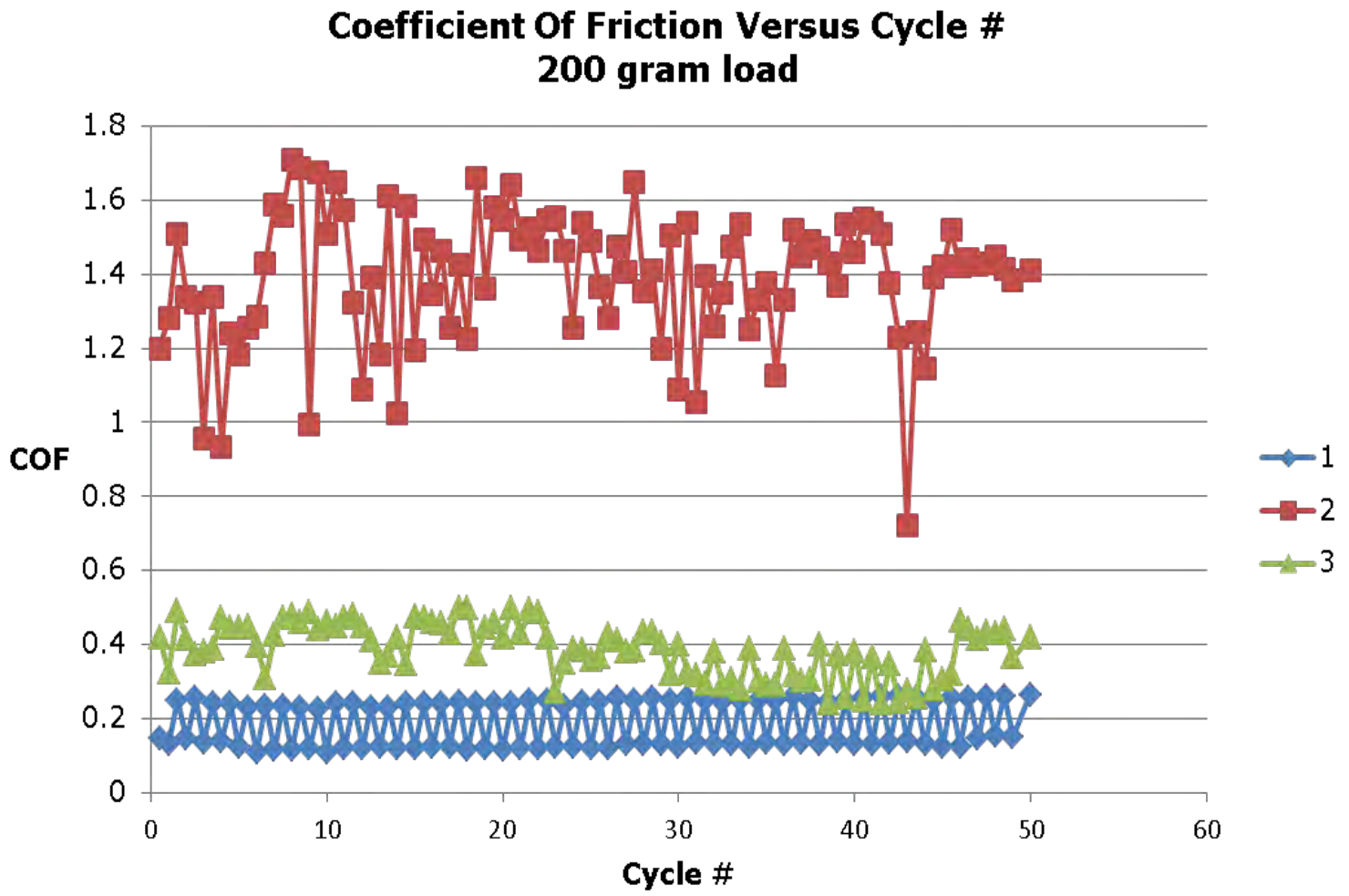
Non-CN Hard Au Process Evaluations
Deposit Hardness, Processes 1-3

Deposit #1: 130 Knoop
Deposit #2: 125 Knoop
Deposit #3: 266 Knoop

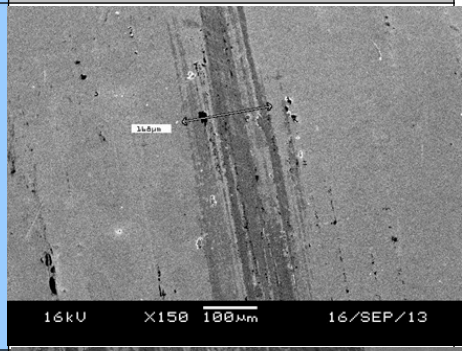
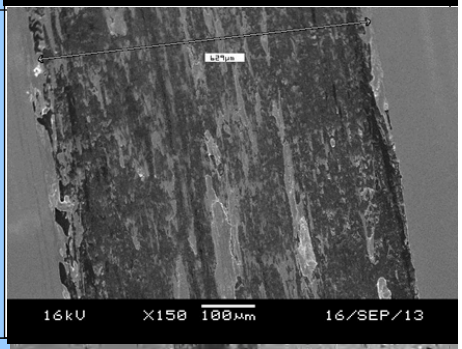
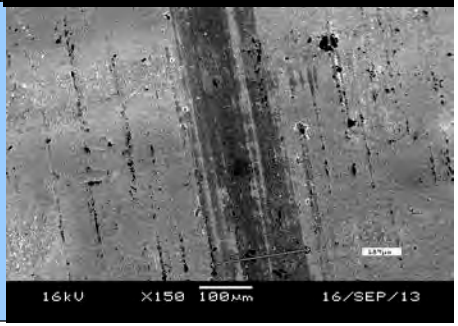
Non-CN Hard Au Process Evaluations Contact Resistance – Processes 1-3



Non-CN Hard Au Process Evaluations Wear Resistance – Processes 1-3



Non-CN Hard Au Process Evaluations
Wear Track Analysis – Runs 1-3

DOE Run #/ Parameters	Track Width (µm)	SEM Photos 150x
Run #1/ 60 µ-in Ni + 30 µ-in Au (PGC)	168	
Run #2/ 60 µ-in Ni + 30 µ-in non-CN Au Rev. I	629	
Run #3 60 µ-in Ni + 30 µ-in non-CN Au Rev. II	189	

Non-CN Hard Au Process Evaluations
Corrosion Resistance(I): NAV Testing

2 hr. NAV Results:

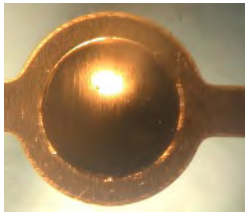
Run #	Porosity
1	0
2	0
3	0

NAV Photos:

1

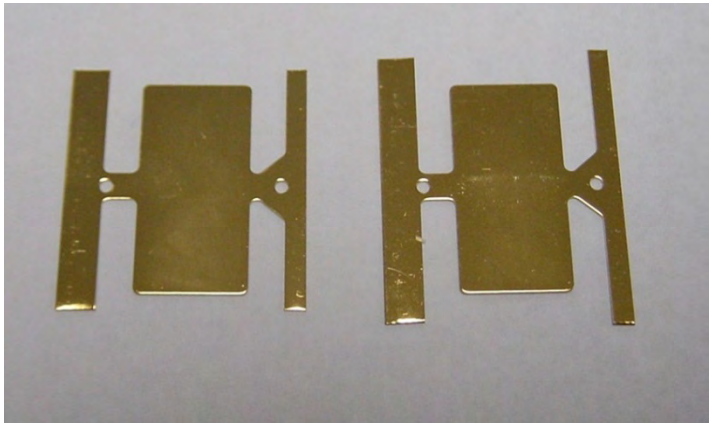
2

3

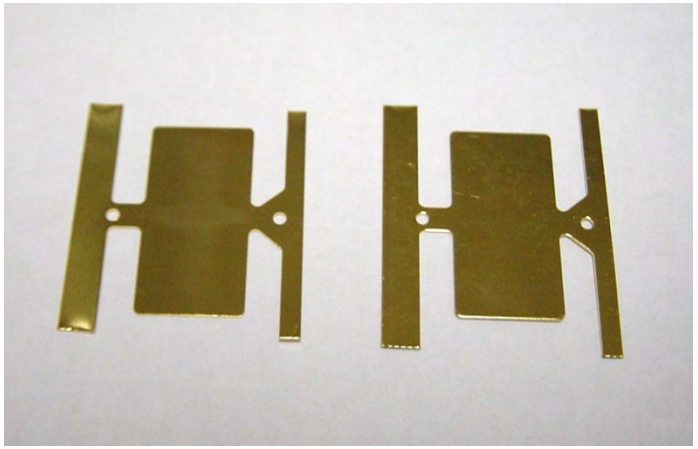


No porosity observed on any samples after 2 hour NAV corrosion test

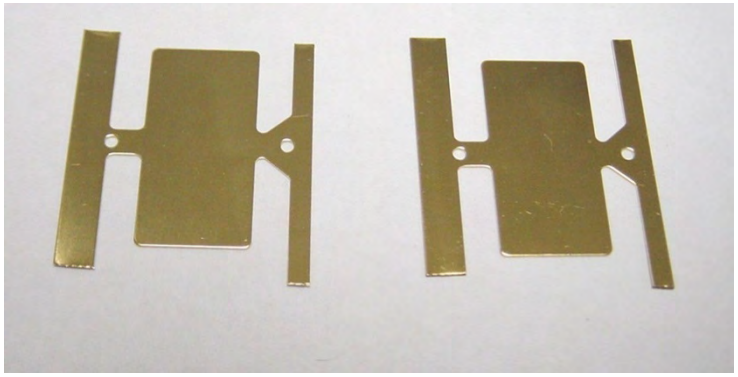
Non-CN Hard Au Process Evaluations Corrosion Resistance(II): MFG Testing



As-plated **#1** After 5-day MFG testing



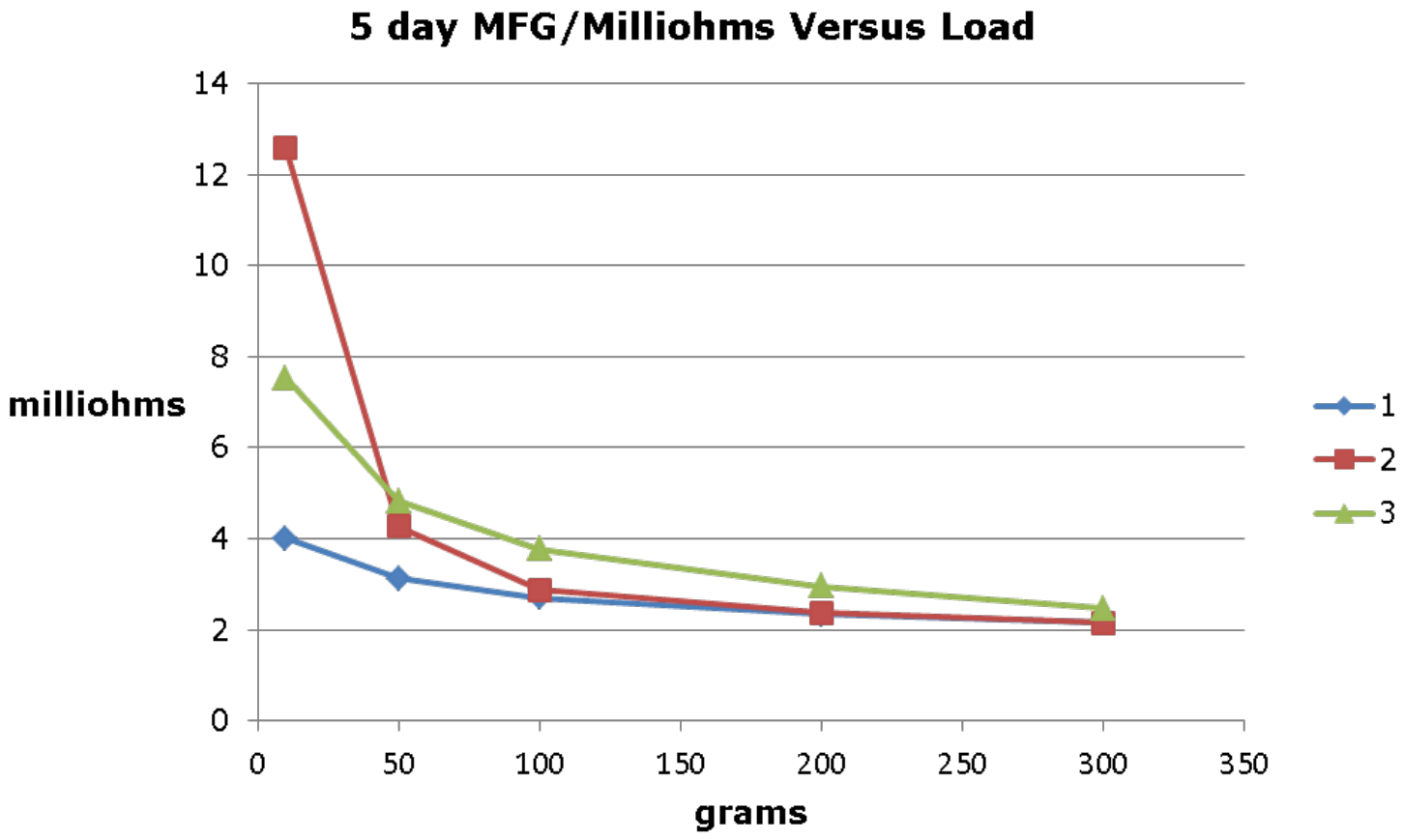
As-plated **#2** After 5-day MFG testing



As-plated **#3** After 5-day MFG testing

No corrosion observed on any samples after 5 day MFG corrosion test

Non-CN Hard Au Process Evaluations Contact Resistance after 5 days MFG exposure – Runs 1-3



Non-CN Hard Au Process Evaluations Deposit Properties: Observations

- Corrosion studies indicated all samples passed the 2 hour NAV test, and all samples passed the 5 day MFG exposure test
  - In addition, all samples exhibited satisfactory CR after 5 days MFG exposure
- Conclusion:
  - All properties of non-CN Hard Au deposits are similar or equivalent to hard Au from PGC solutions with the exception of wear resistance, in which case a higher Ni content is required in the non-CN Au deposit to obtain equivalent wear performance.

Non-CN Hard Au Process Evaluations Conclusions

- Deposits produced from Process #3 (Non-Cyanide Rev II) offer comparable performance to PGC gold deposits in all functional areas, however…
- Co-deposited nickel concentration for Process #3 exceeds traditional conventional limits for hardness (266 Knoop) and purity (1.5% Ni) in gold deposits
  - Industry standard Type I Au = max. 0.3% Ni and Grade C = hardness range of 130-200 Knoop
    - Above standard is based on US Military Specs…is it applicable to consumer products?
- Non-CN Au appears to be a viable option for connector reel-to-reel applications based on the results of this study, assuming concerns of purity and hardness can be overcome
  - Flash Au over PdNi is another option

Non-CN Hard Au Process Evaluations
Final Words

- Nobody knows for sure if/when PGC will be banned in China and/or other countries
  - Latest round of NDRC meetings on this subject took place in Beijing May 21, 2014
  - Conclusion: NDRC confirmed that the ban on PGC is suspended; industry experts expect that nothing will happen for next 1-2 years
- While non-CN hard Au for high speed electronic connector plating applications remains a challenge, the solution presented in this paper shows promise as a potential non-CN hard gold replacement

Acknowledgements

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