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Thermal Desorption Spectroscopy of Gold Plating for Tritium Thermoelectric Generators

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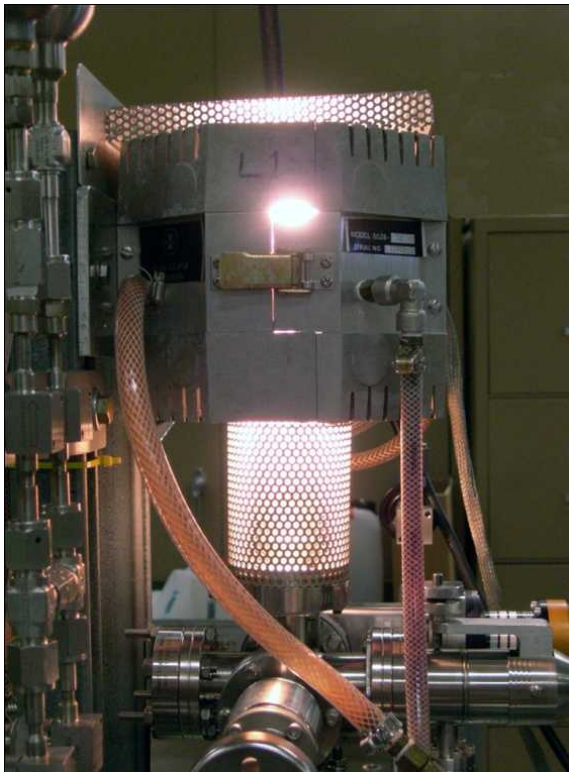
Goal

Requirements for TTG gold.

- Function at elevated temperature (e.g. 250^{o}C).
- Minimize heat loss through:
  - Conduction--minimize outgassing.
  - Convection--minimize outgassing.
  - Radiation-- minimize emissivity (ε).
- Have adequate adhesion.
- Do all this for years.

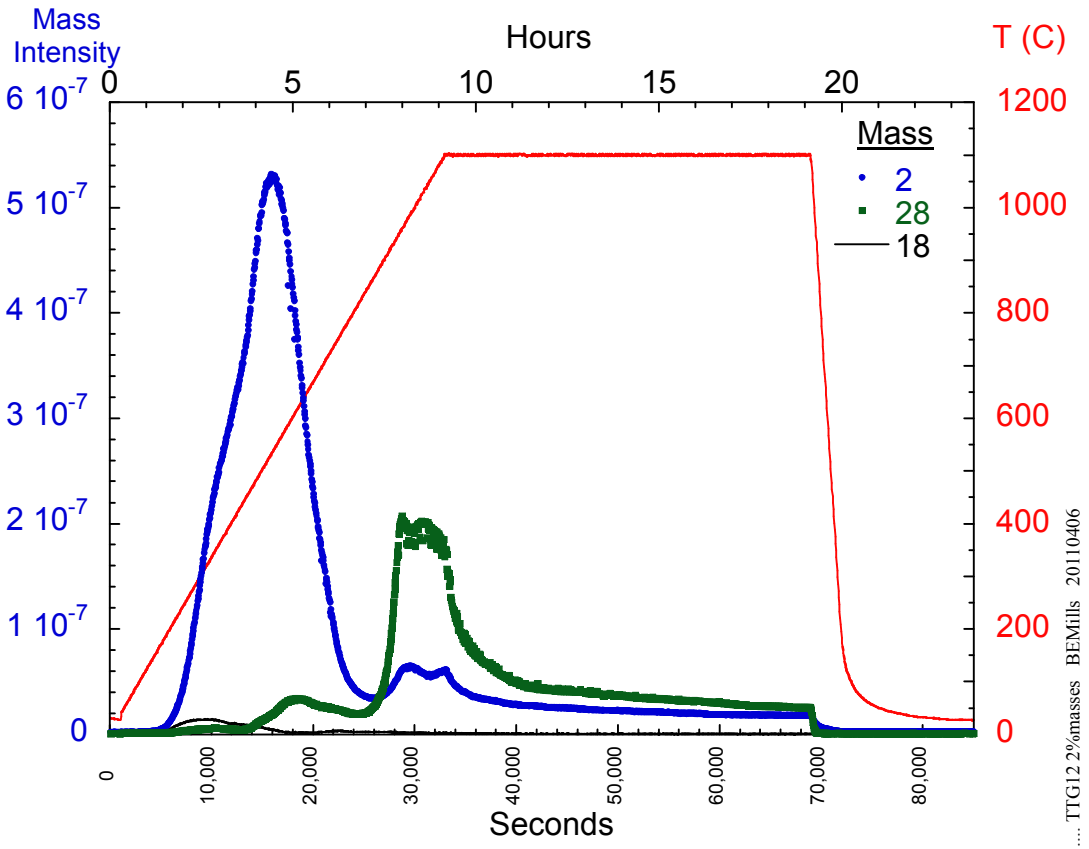
Thermal desorption system.



→ Sample can be heated up to 1450°C in vacuum while monitoring mass spectrum of evolved gasses.
→ We can look for mass 2 through 300; this work 2 through 100; saw no species above 44 amu.

TDS 304L

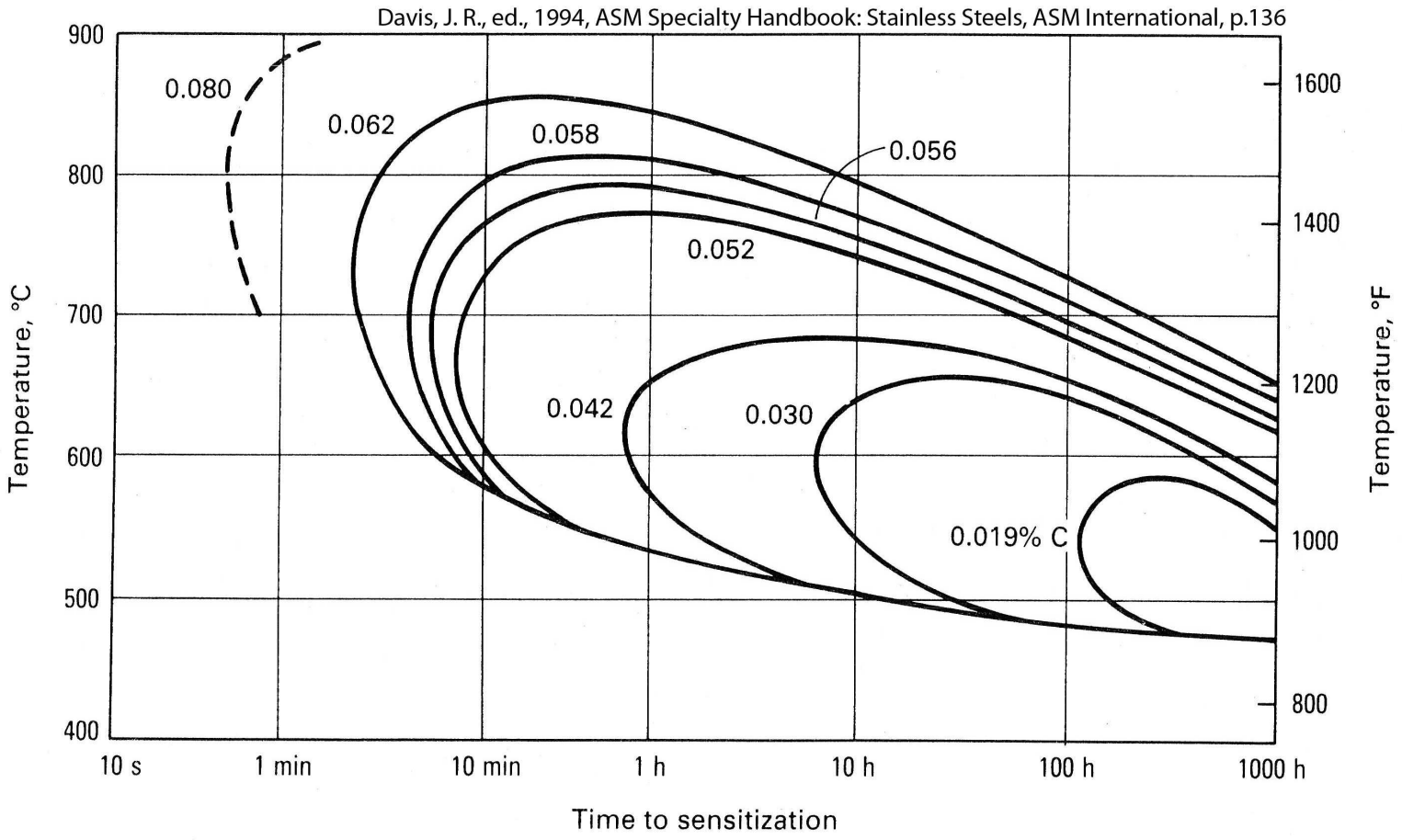
Two temperature ranges for degassing.



2K/min to 1100°C gives us an overview of degassing. 1100°C is a typical annealing temperature and not acceptable for retaining forging properties.

TTS 304

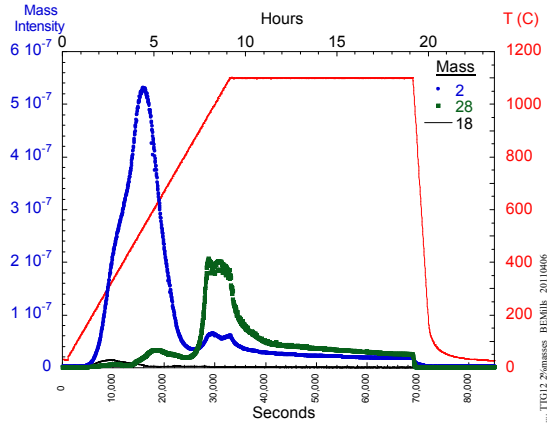
Time-temperature-sensitization.

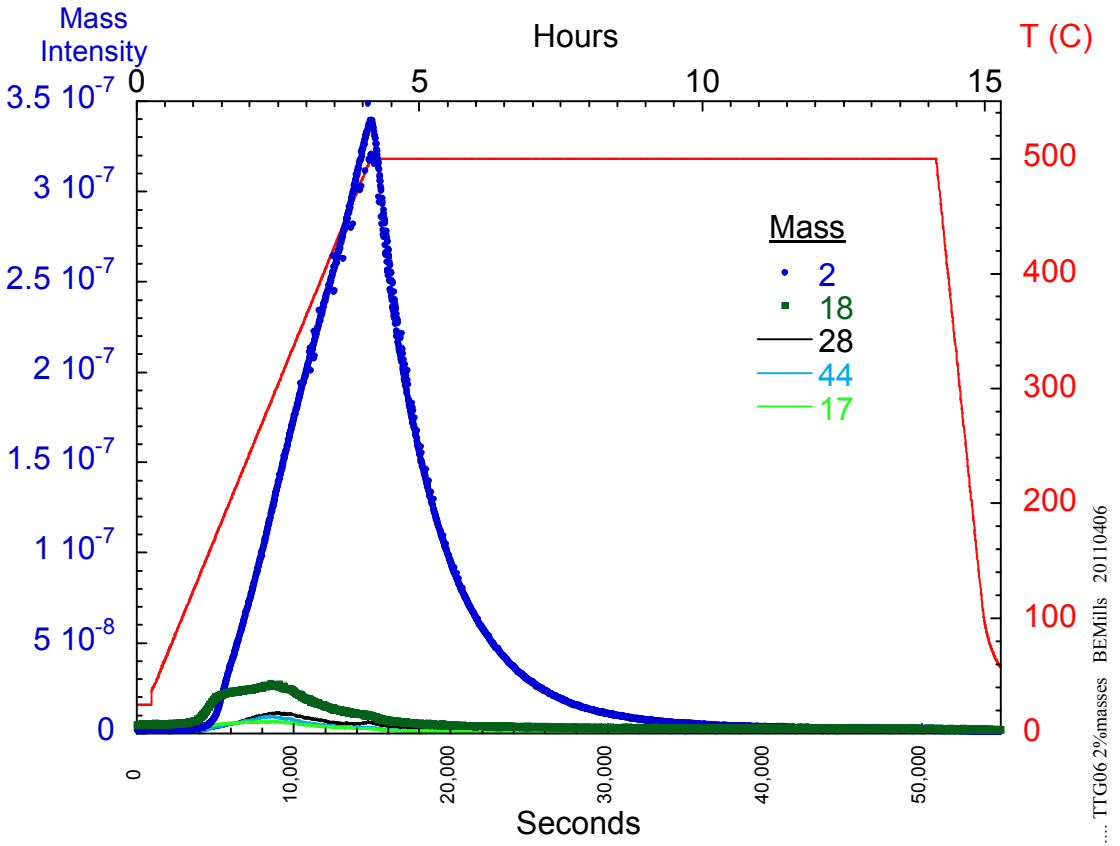


TTS curve for 304 stainless steel. Maximum allowable carbon in 304L is 0.030%, meaning that there is no carbide precipitation before 25 hours at 500°C.

TDS 304L

A 500°C degas is done in 10 hours.

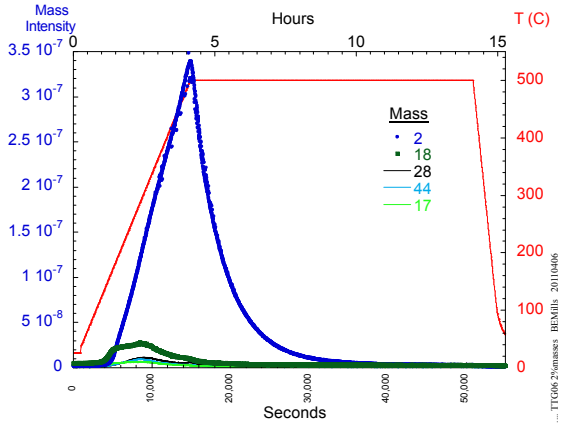


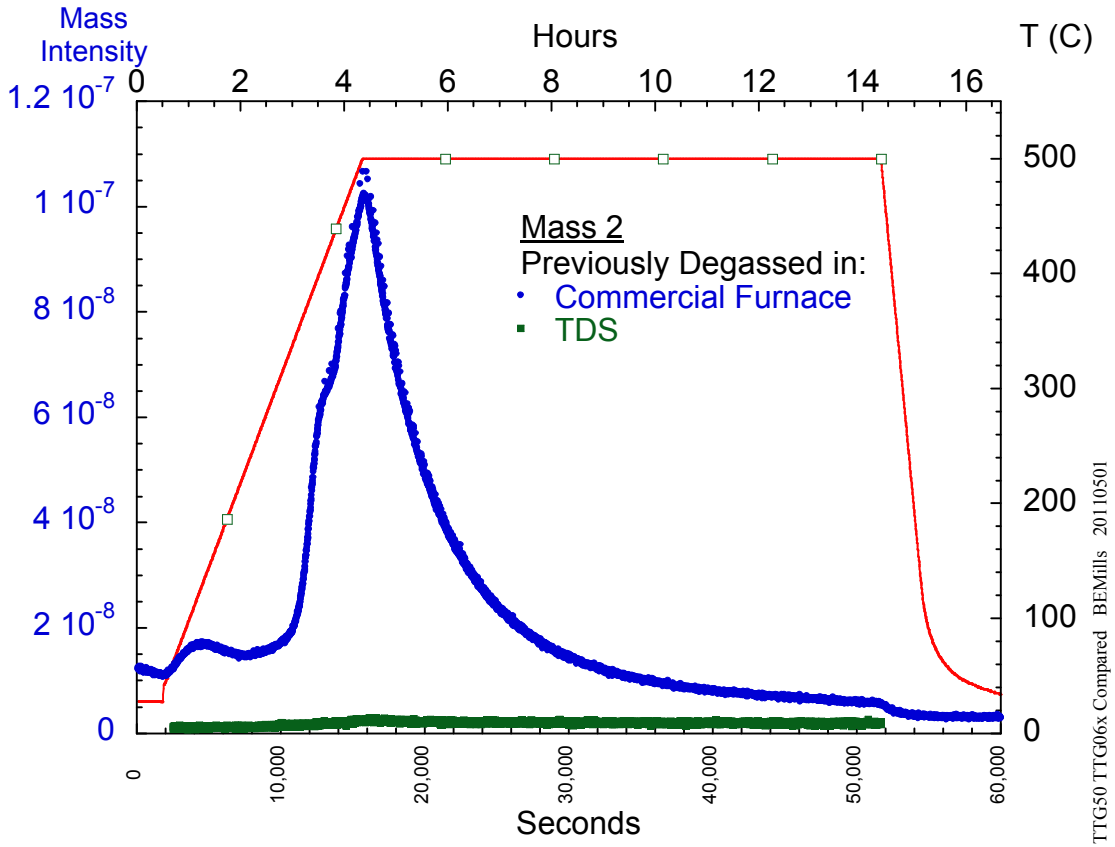


At 500°C hydrogen is the most abundant and tenacious species. In 10 hours essentially all outgassing is finished.

TDS 304L

Inadequate time/ temperature control.

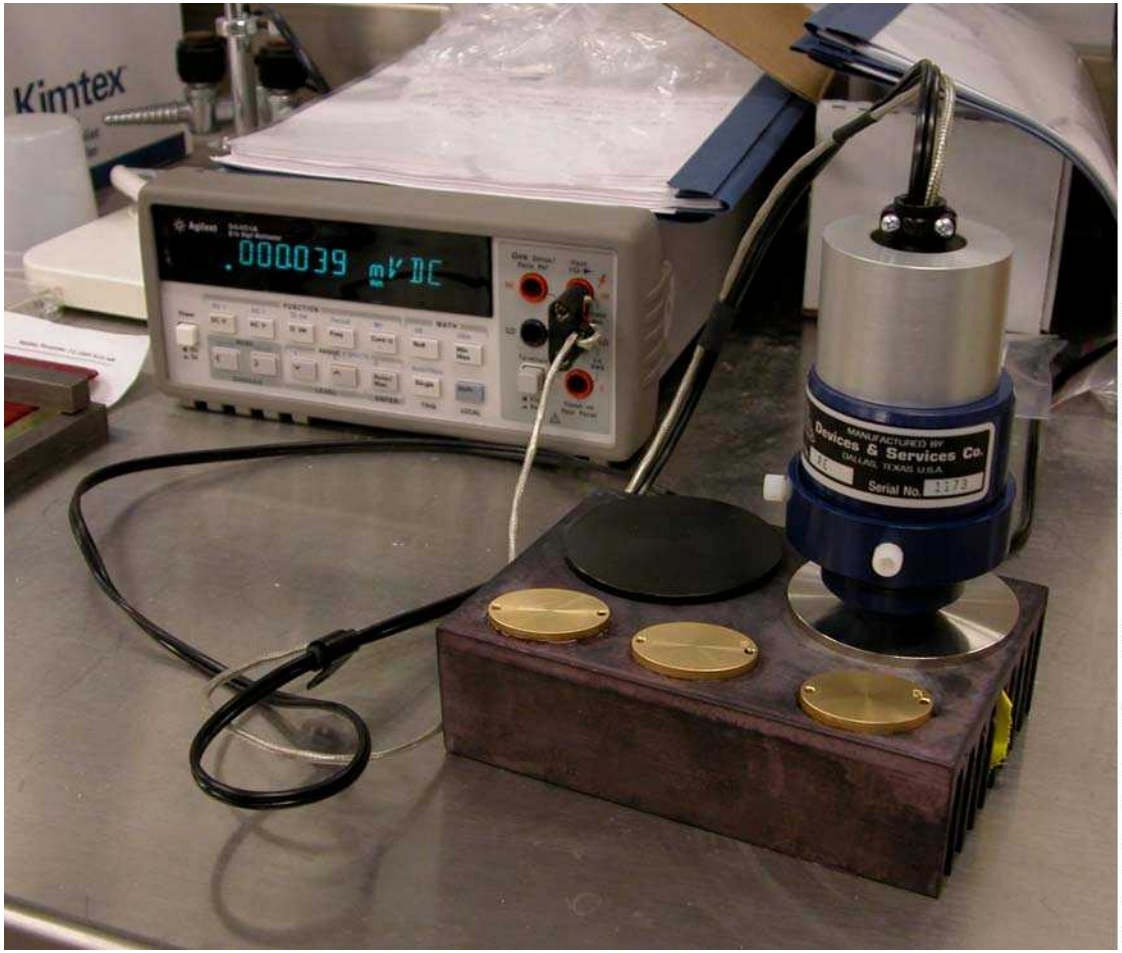




A number of coupons were inadequately outgassed at a commercial vendor.
It would be wise to retain control of vacuum, time, and temperature .

ε

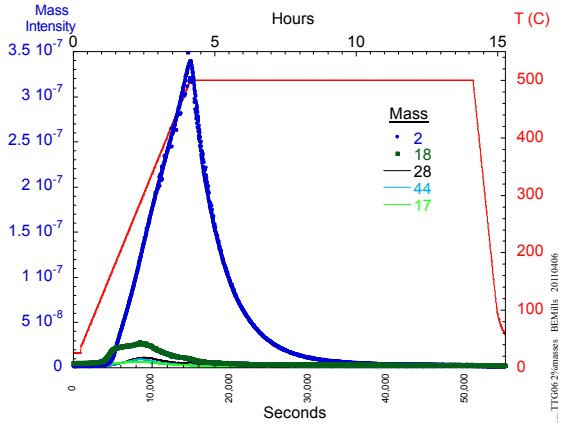
Emissivity measurement.



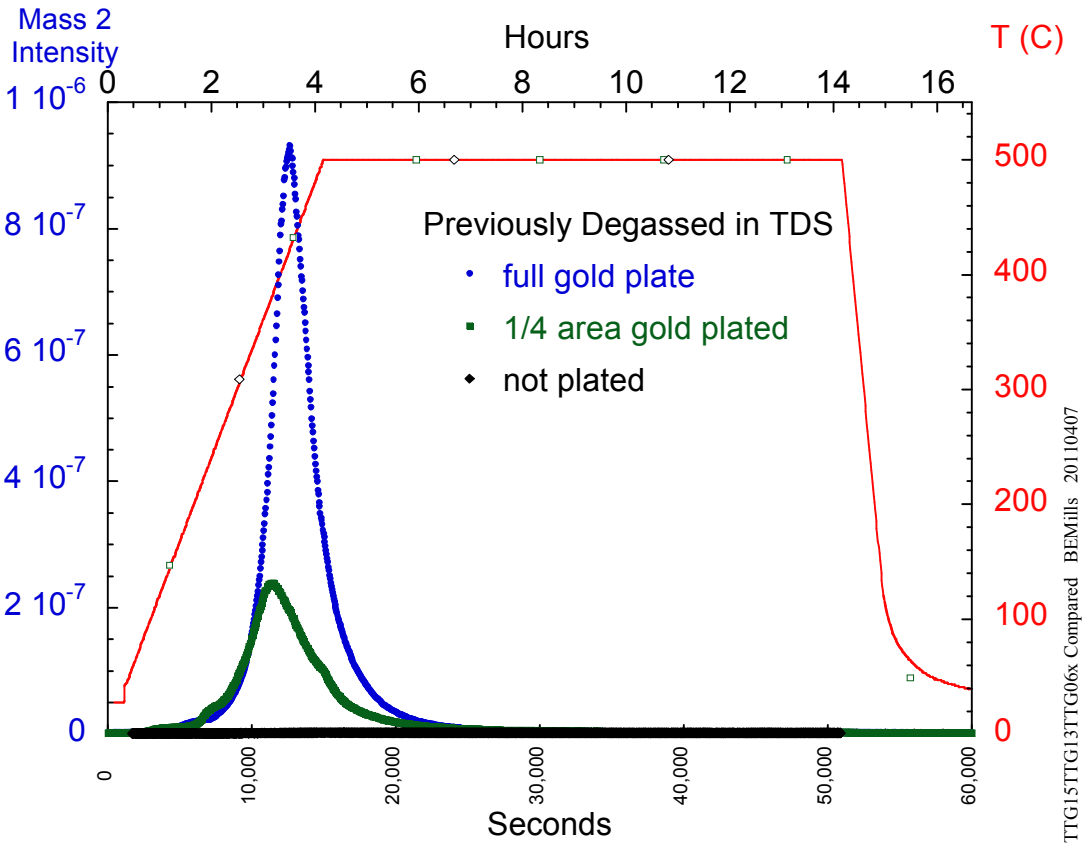
Emissivity Setup Pic ANissen/BEMills 20110505

To use the smaller sample we have, the detector is fitted with an adapter.

Gold plating adds hydrogen.



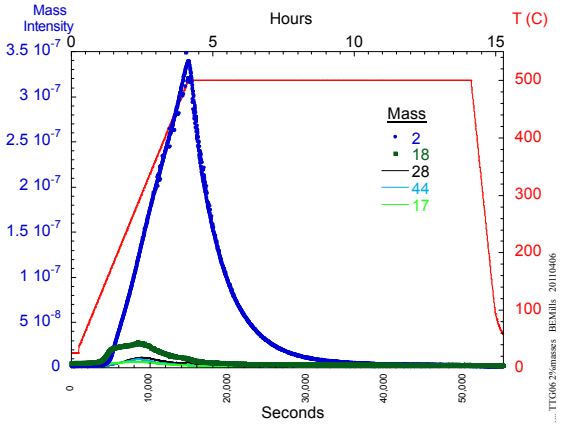
0.031 ε

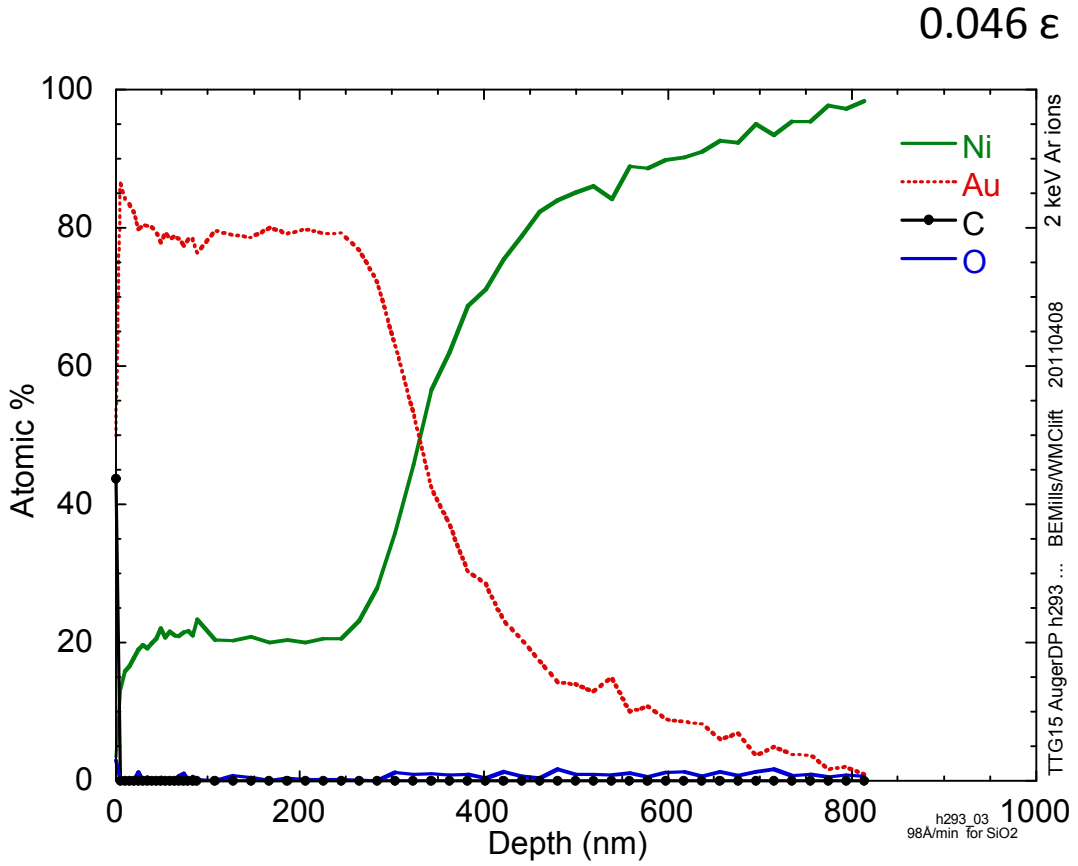


Partially plated coupons outgas more easily than fully plated coupons.
Both outgas more easily than 304L stainless steel.

500°C vacuum

Auger Depth Profile 500°C/10 hours.



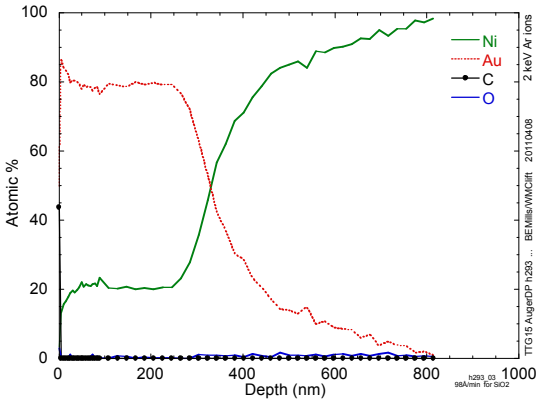


Once the coupon is completely degassed, the nickel has reached an almost uniform concentration of 20% in the gold layer.

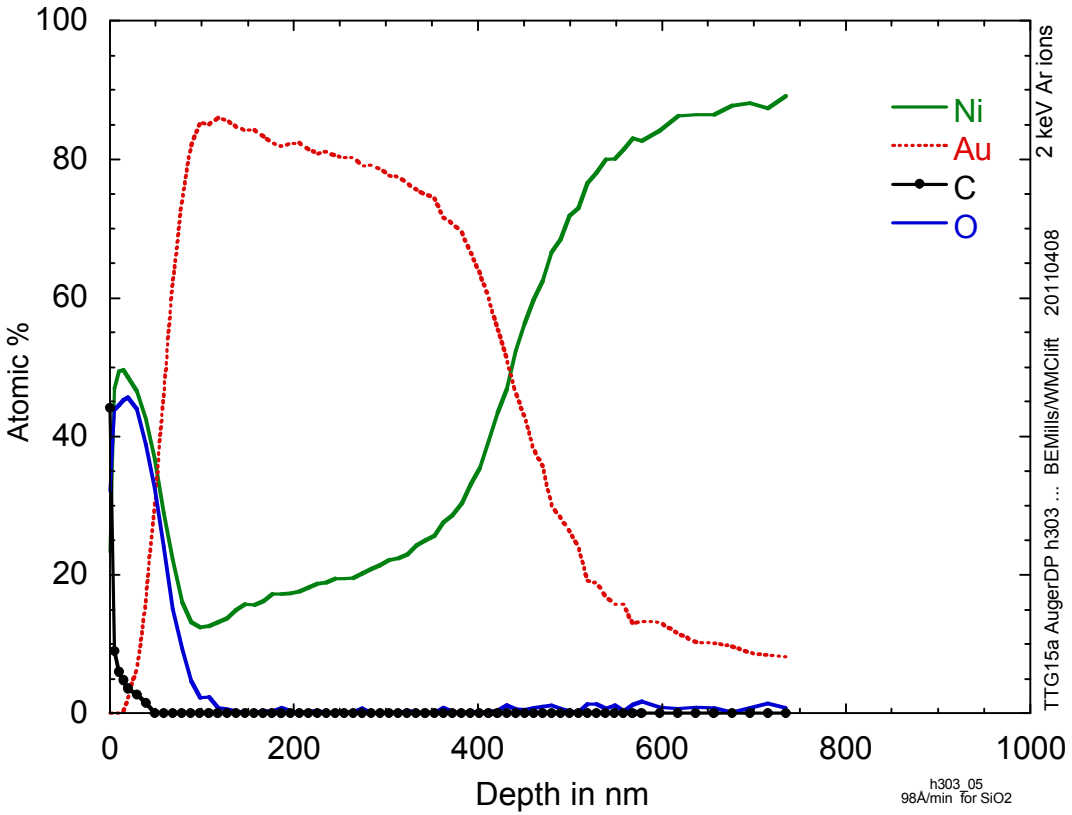
500°C air

+500°C/10 min in air.

0.046 ε



0.043 ε

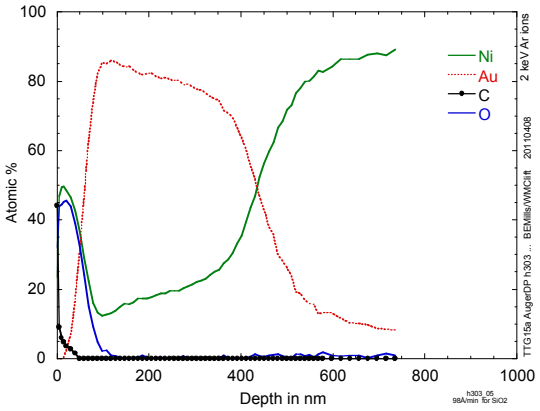


Quick heating and cooling causes a localized depletion of Ni in Au as it diffuses to the surface to react with oxygen in the air.

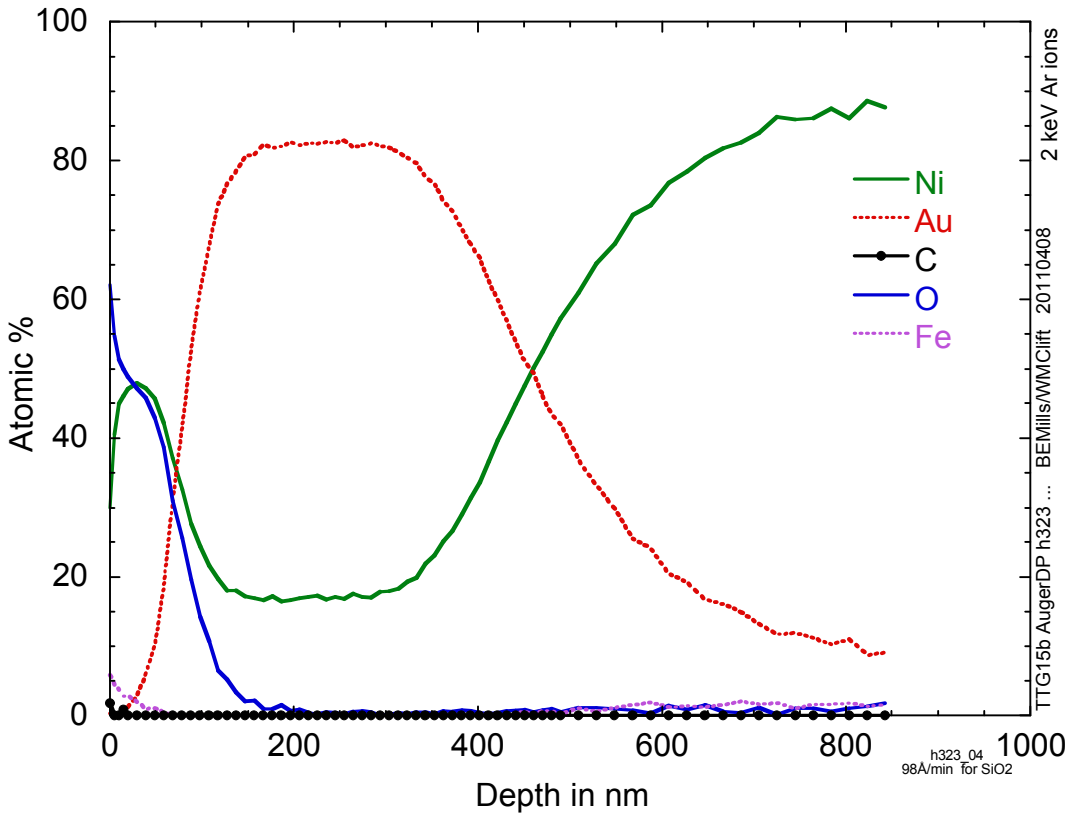
500°C air

+500°C/1 hour in air

0.043 ε



0.055 ε

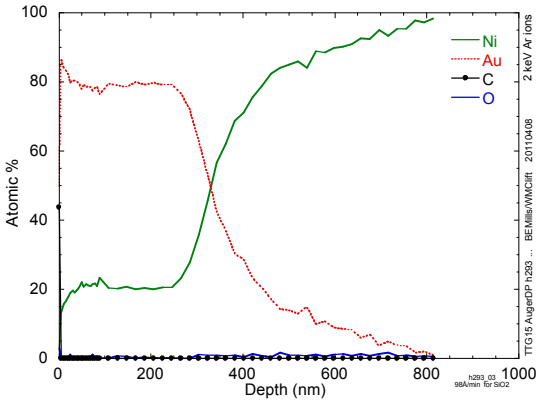


Further heating in air returns the concentration of Ni in the Au to 20%, has little effect on oxide thickness, and brings Fe to the surface to oxidize.

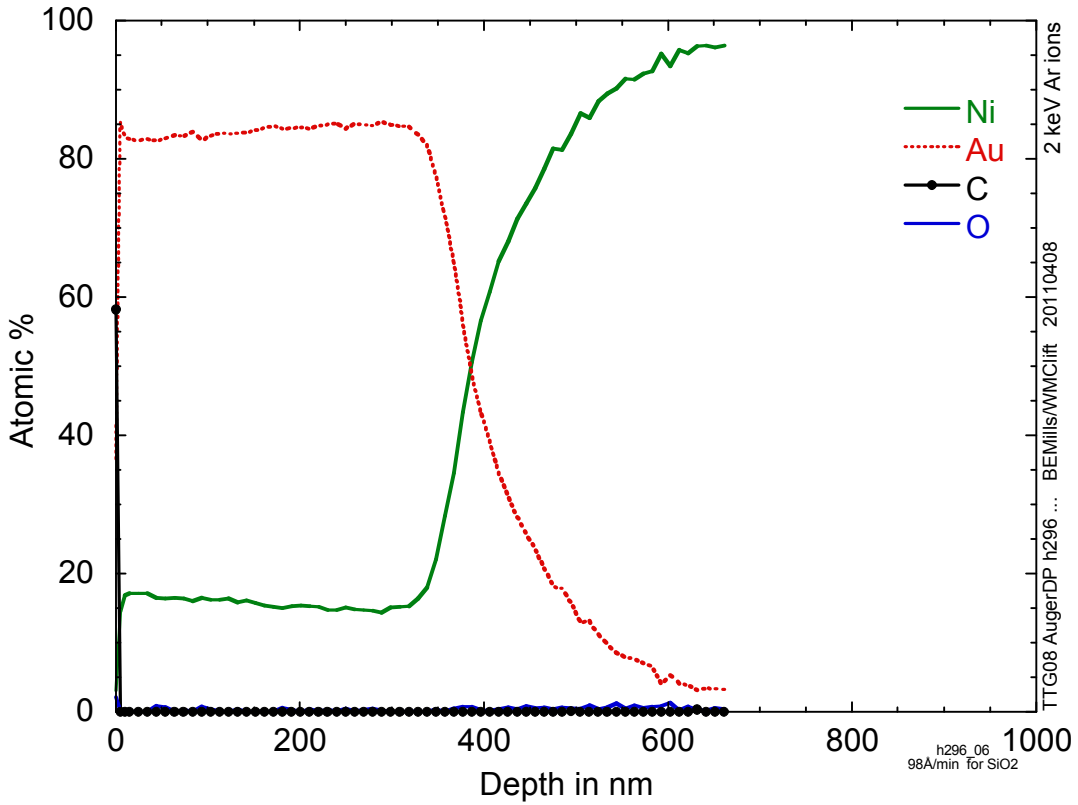
400°C vacuum

400°C compared to 500°C

0.046 ε



0.051 ε

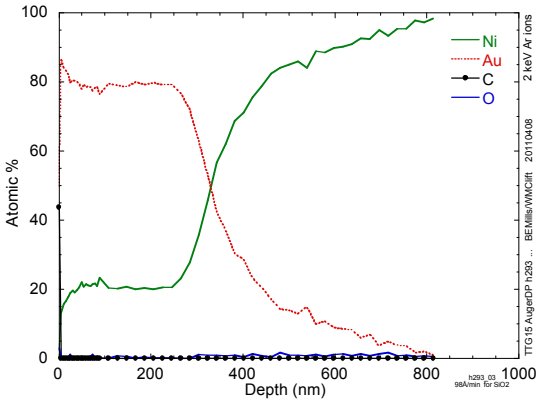


Although the concentration of Ni in Au after a 400°C vacuum treatment is less at ~16%, the emissivity is not improved from 500°C.

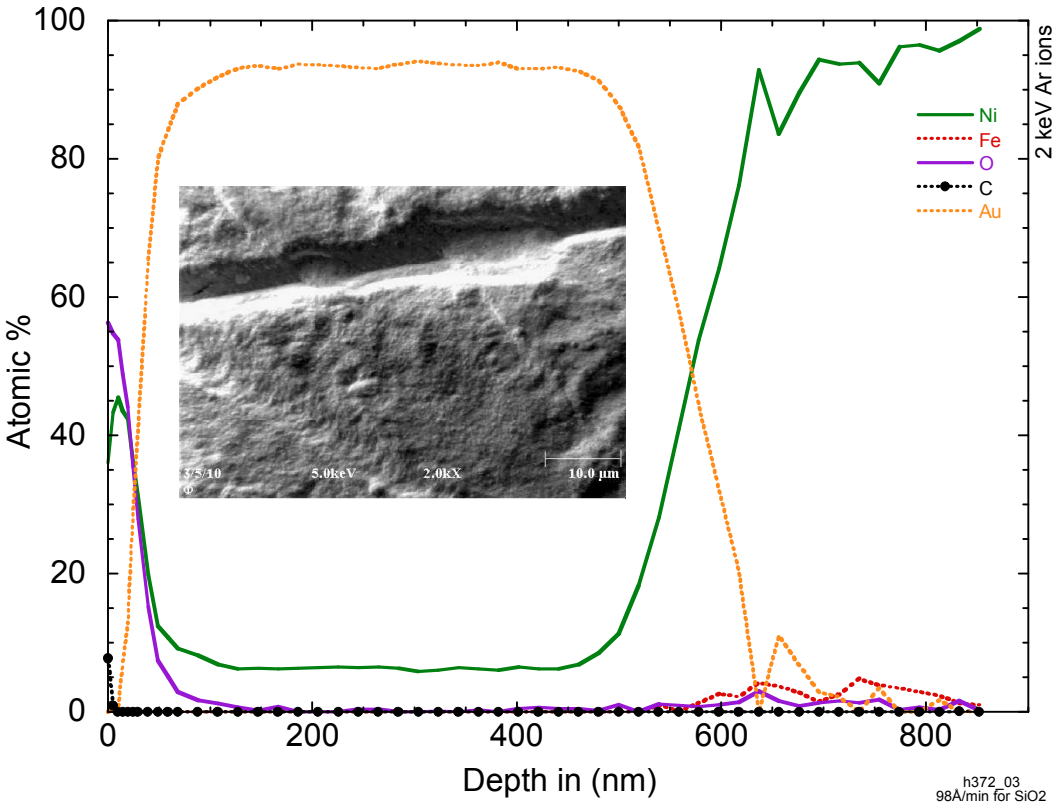
300°C air

300°C/13hr vacuum; I week air.

0.046 ε



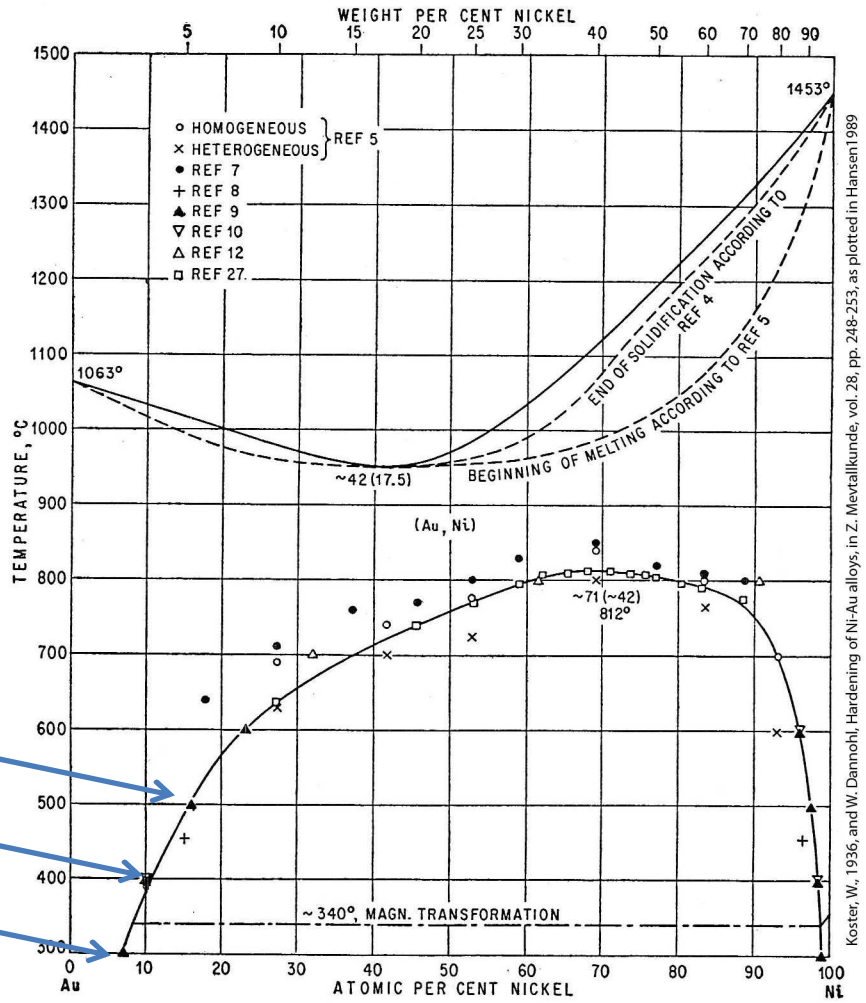
0.032 ε



300°C vacuum treatment stopped when the hydrogen signal dropped to 10% of the peak shows no measurable change in emissivity even after one month at 300°C in air.

Au/Ni

Ni solubility in Au.



Koster, W., 1936, and W. Dannohl, Hardening of Ni-Au alloys, in Z. Mevtallkunde, vol. 28, pp. 248-253, as plotted in Hansen1989

500°C

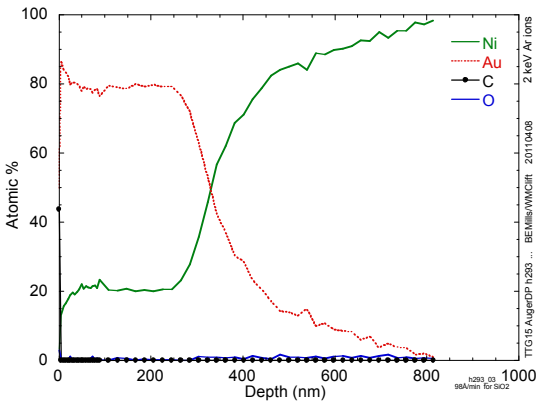
400°C

300°C

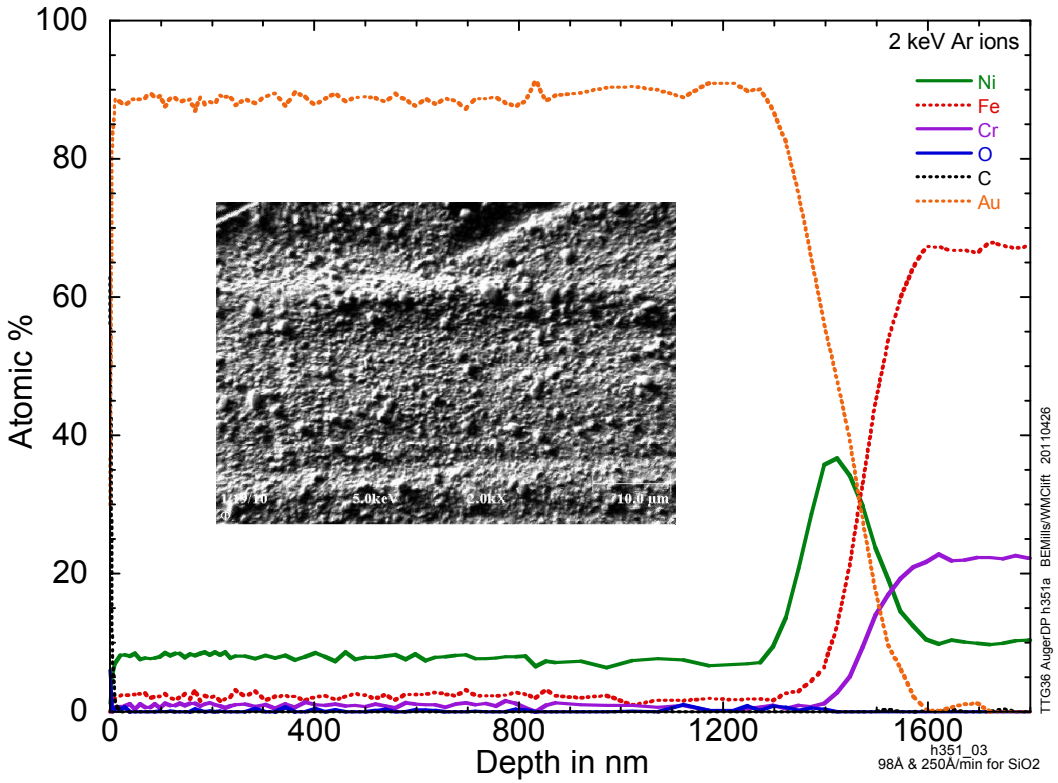
The trend of solubilities in this work is consistent with that seen in the literature.

Diluting the nickel in the gold layer.

0.046 ε



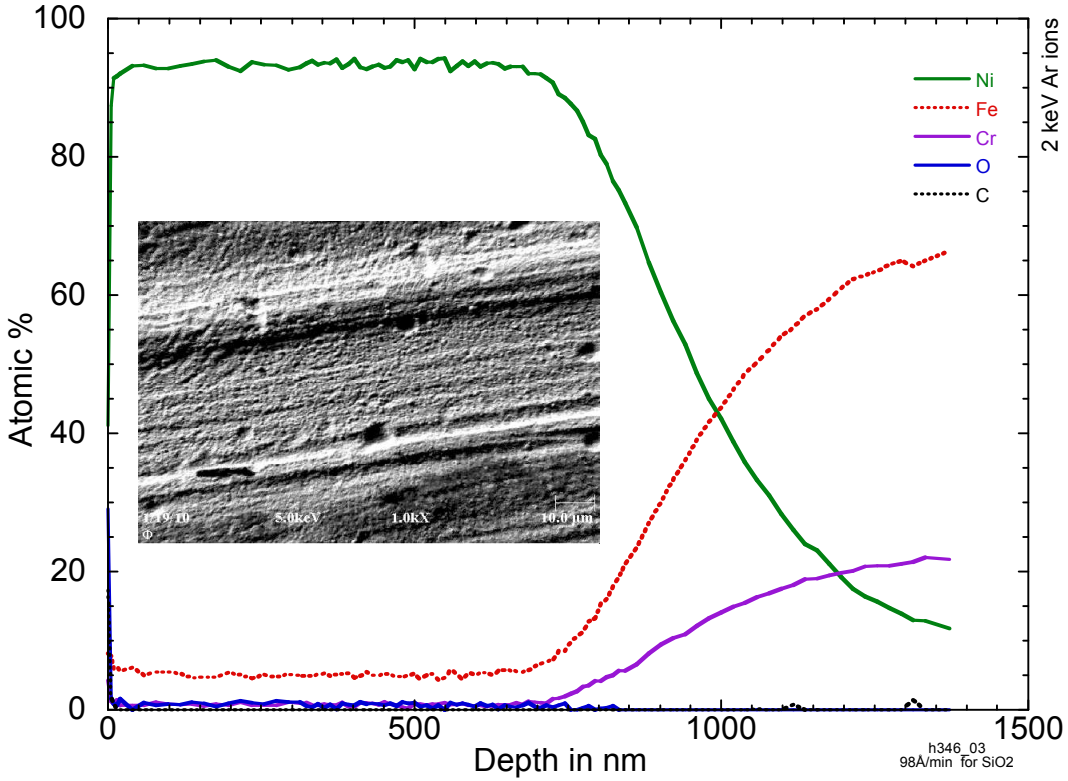
0.092 ε



Ni $^{1}/_{5}$ thickness; Au 3X thickness. This Au layer contained about 8% Ni, 2% Fe, and 1% Cr. It has the highest emissivity in this work.

2 degases

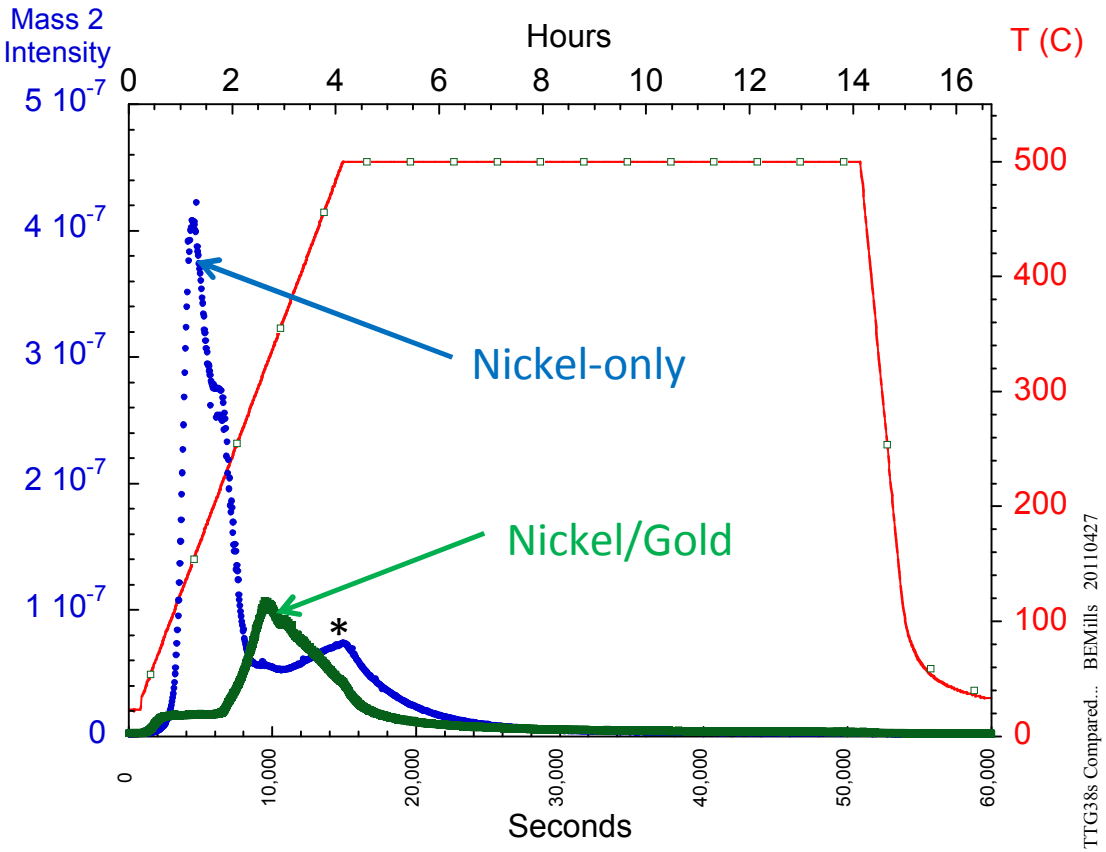
Nickel-only layer 500°C/10 hours.



The concept was to degas the nickel before adding the gold.

2 degases

Nickel-only and Ni/Au compared.



H2 comes out of Ni easily. But when gold is added, more H2 is also added.
Part would need to be masked and fixtured twice.

* This hydrogen is the residual from incomplete commercial degassing.

Plating fixture

For many parts a fixture is used.

DSCN0251 plating fixture with 6 TTG coupons BEMills/JTHachman 20110503

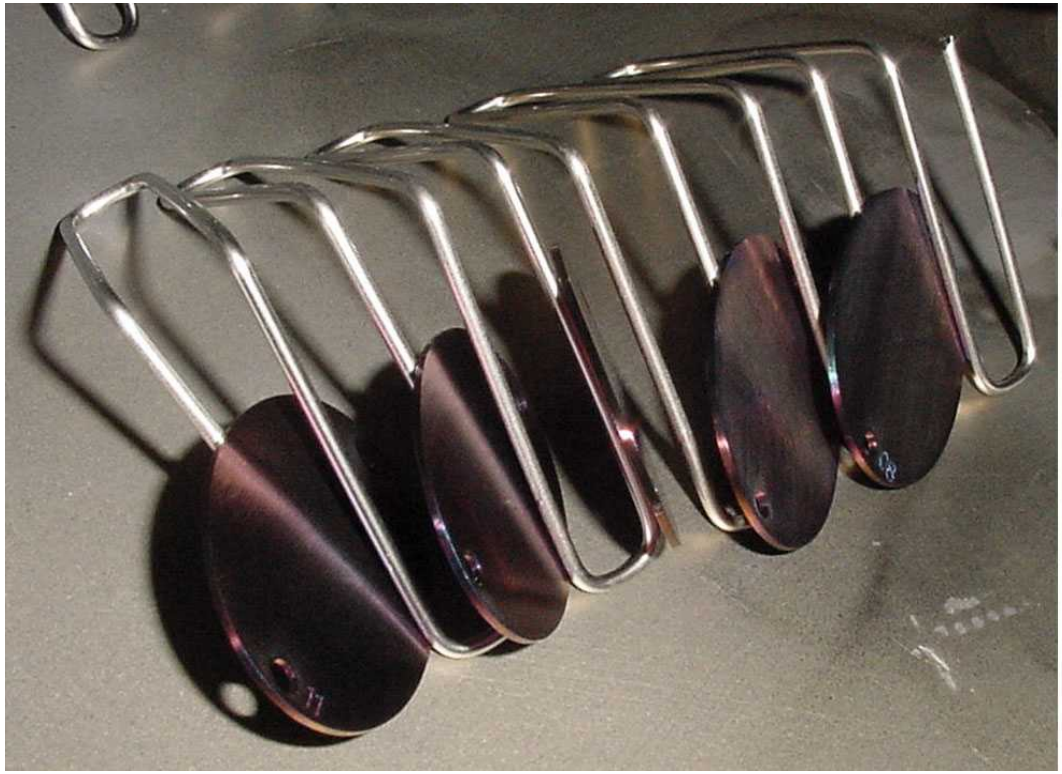
A place on the part with screw threads that can be used for both hold the part and making electrical contact is ideal.

If possible the attachment point should be in an area that is not to be plated.

Degas fixture

TDS and Brew furnace fixtures.

MVC-218F TTG Coupon in TDS BEMills 20110502



MVC-215F TTG coupons in Brew Furnace BEMills 20110502

Fixtures should allow the best exposure for radiation transfer.
Measured temperature should reflect interior temperature of part.

Conclusions

- Unplated parts should be degassed at 500°C for up to 24 hours.

  24 hours should be used if it is not possible to monitor outgassing.

- Plated parts will retain good emissivity if degassed at 300°C.

  24 hours is recommended for this process as well.

  Ring shear tests (not reported here) show adhesion is slightly enhanced through baking.

Questions?

Plating Process

- Caustic cleaning using Oakite 90 at 155˚F for 15 min.
- DI (deionized) water spray rinse.
- Nitric acid, 30% by volume, dip at RT (room temperature) for 30 sec.
- DI water spray rinse,
- Blow dry with dry nitrogen.
- Use stop-off lacquer and/or tape to mask areas that should not be plated.
- Reclean and rinse if needed as the part surface may have been contaminated during previous step.
- Anodic etch in 30% sulfuric acid and 150 ASF (Amps per square foot) at RT for 3 min.
- DI water spray rinse.
- Woods Nickel strike at 50 ASF for 5 min. at RT.
- DI water spray rinse.
- Gold plate in gold-cyanide bath* at 1.5 m/cm2 for 10 min. at 120^{o}F for 1 micron.
- DI water spray rinse.
- Blow dry with dry nitrogen.

Plating Solution

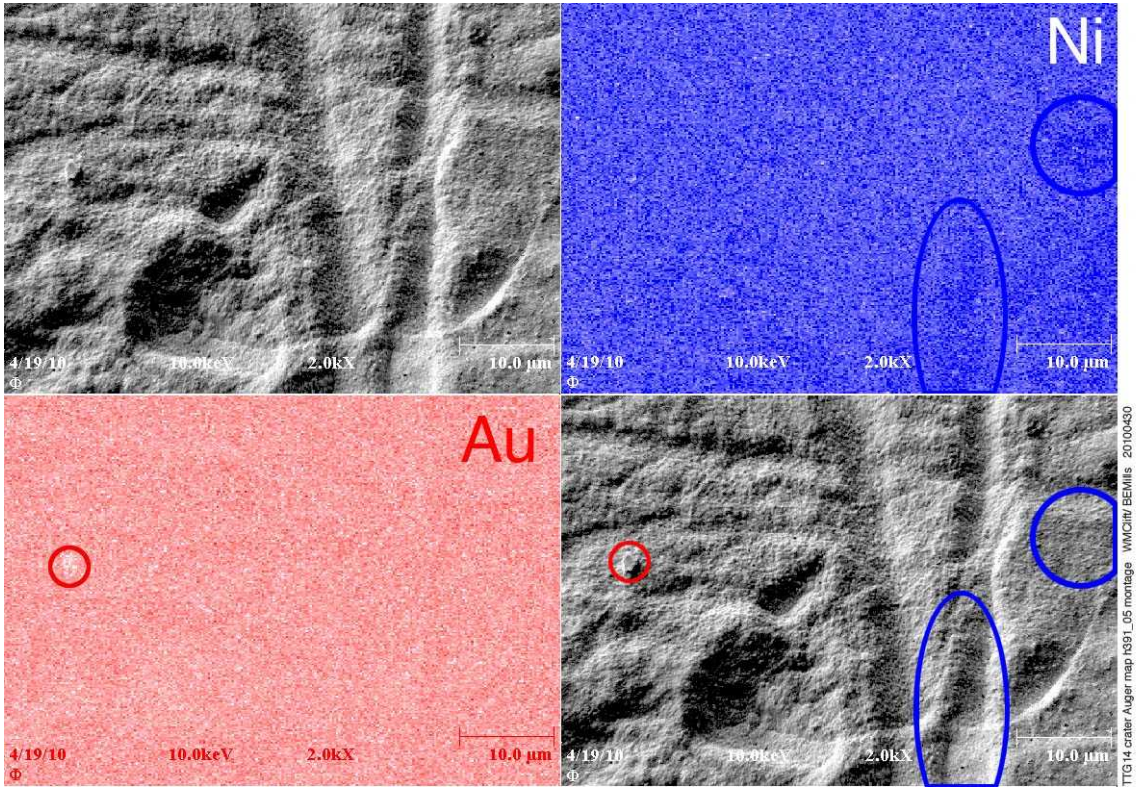
For a 10 liter bath use:
750ml DEQUEST 200LC
10 oz. gold potassium cyanide
9250 ml water

Adjust the pH when needed to 4.5 using DEQUEST solution.

Woods Nickel Solution

Nickel Chloride – 240 g/l
Concentrated HCl – 125 ml/l

Auger Map of +300°C I week air.



Since surfaces of the coupons were intentionally rough to promote adhesion, Auger depth profiles needed to be done on small areas, which can have anomalous concentrations.

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