

Novel and Innovative Non-Cyanide Silver Process: A Report on Commercial Plating Experiences

by Sascha Berger* & Gerhard Hoffacker

Plating solutions for depositing precious metals like silver or gold are still predominantly based on cyanide or sulfite compounds. Many attempts have been aimed at the deposition of silver from cyanide-free solutions. Existing alternatives hitherto applied, such as thiosulfate-based silver baths pose serious problems regarding bath stability and have also failed to achieve success in actual practice. A new type of electrolyte now makes it possible to carry out silver-plating from a cyanide-free solution under industrial production conditions.

Conventional silver plating

Even today, silver electroplating from aqueous electrolytes is still based almost exclusively on the use of potassium silver cyanide [KAg(CN)₂]. In addition, these electrolytes contain, to some extent, well over 100 g/L (13.4 oz/gal) free cyanide for precious-metal complexing purposes, for controlling macrothrowing power and for increasing conductivity. Conventional barrel and rack plating cover both functional and decorative fields of application.

Silver coatings are required for their specific properties in various applications. For technical purposes, properties such as low contact resistance, resistance to corrosion and tarnishing, solderability and sufficient adhesion are of fundamental importance. Coatings suitable for such purposes exhibit a semi-bright or dull finish and possess

microhardness values ranging from 70 to 100_{VHN}. They can be obtained from electrolytes containing low quantities of grain refining agents as well as brightening and hardening agents.

Apart from brightness properties, the white shade of the silver coating is of vital importance for decorative purposes. In order to obtain the desired grade of brightness as well as the required microhardness of up to 150_{VHN}, organic or metallic compounds containing antimony and arsenic are added.

Cyanide-free silver electrolytes

The development of cyanide-free processes has progressed with the aim of bringing about improvements in the handling of these electrolytes from the standpoint of safety, waste water treatment and environmental regulations. Attempts have been made in the past to replace extremely toxic cyanide processes with low-polluting, non-toxic ones.

These efforts have involved research and development on non-cyanide compounds such as silver nitrate, silver iodide, silver rhodanide, silver pyrophosphate and the silver chloride-sodium thiosulfate system.^{1,2} In addition, silver complexes of organic acids (propionic acid and acetic acid) or inorganic acids such as pyrophosphoric acid and sulfamic acid have been considered.³ The best results have been obtained using iodide or thiosulfate as ligands.⁴ Of these, however, only the thiosulfate electrolyte has succeeded in attaining any technical importance, albeit negligible, owing to its limited stability. In 1975, Culjkovic, *et al.*⁵ developed a thiosulfate-based electrolyte for bright silver-plating of rack and bulk articles. Compared to processes containing cyanide, this electrolyte exhibited comparably good throwing power. The resulting depos-

Nuts & Bolts: What This Paper Means to You

Cyanide replacements have been developed for many of the plated metals, but some have come more easily than others. Silver has been one of the stubborn ones in yielding its secrets of economical and viable non-cyanide plating chemistry. Here, the authors describe a new electrolyte that allows silver-plating from a cyanide-free solution, including experience with an industrial scale tryout.

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its had good electrical conductivity as well as good tarnishing resistance. In 1989, Sriveeraraghavan, *et al.* reported a thiosulfate silver plating solution described as being "fairly stable," yielding adherent deposits over copper only.⁶ No mention was made of the appearance.

In 1978 and 1981, Hradil *et al.* patented a non-cyanide silver plating solution based on a succinimide complex.⁷ Jayakrishnan, *et al.* provided information on a silver plating solution based on a succinimide complex as well in 1996.⁸ This solution contained silver, potassium carbonate and succinimide. Hull cell experiments indicated that a smooth, white silver deposit was possible. However, the deposit was not bright and no data on adhesion was reported. In 1998, Masaki, *et al.* reported a mirror-bright silver plating deposit from a non-cyanide solution containing silver, succinimide, boric acid (as a buffer) and polyethylenimine (PEI).⁹ The PEI was added to allow a higher applied current density up to 2.0 A/dm² (18.6 A/ft²) and yield a mirror bright surface. No adhesion data was reported. To our knowledge up to now, there is no non-cyanide silver plating process commercially available which meets all desired requirements regarding the solution as well as the silver deposit.

CMFI investigation

In 2002, the Chicago Metal Finishers Institute (CMFI) made an investigation on non-cyanide silver as a substitute for cyanide processes. The results were submitted to the Illinois Waste Management and Research Center and published as a WMRC report.¹² The study was conducted with two commercially available processes to determine if recent non-cyanide silver plating processes could be a possible replacement for cyanide based formulations. The suppliers of these processes were not identified. Three major problems with the non-cyanide silver baths were investigated:

1. Their susceptibility to contamination by immersion deposition,
2. The failure to yield a bright, white deposit and
3. The failure to provide adequate adhesion on bright nickel and copper substrates.

Working with polished brass or bright nickel plated brass, the researchers were unable to remedy all three shortcomings. No single process was found to resolve all three problems.

New cyanide-free silver process

A novel development to emerge from our laboratory is based on the use of albuminate amino acids and their derivatives.^{10,11} The German abbreviation for this family of substances (EAS) was established during the period when our work was ongoing, and it was appropriate to maintain this terminology here. The use of such substances made it possible to deposit practical silver coatings from an electrolyte that dispenses with both cyanide-bound silver and free cyanide. From the start, this eliminated critical problems associated with handling toxic cyanide, *e.g.*, safe working conditions and pollution of wastewater through detoxification with hypochlorite. Nor are hard EDTA-class complexing agents involved, resulting in additional advantages from the standpoint of waste water treatment.

The slightly alkaline, cyanide-free electrolyte yields fine silver coatings. None of the compounds used in the bath contain toxic substances or additional metal ions such as antimony or selenium. The process is currently suitable for functional applications. The EAS electrolyte operates using silver-methanesulfonate (AgMSA), which acts as a metal donor and runs at a pH value of about 9.5 to 10. Laboratory experiments in both the Hull Cell and a 1-L beaker

have revealed an appreciable bright-white silver appearance on brass parts. The applicable current densities range from about 0.3 to 1.0 A/dm² (2.8 to 9.3 A/ft²).

Experimental

Silver plating experiments were carried out using polished brass panels or nickel-plated brass panels in either a Hull cell or a 1-L beaker with agitation supplied with a magnetic stirrer. The anodes were made of silver. The plating was performed for 5 or 10 min with a current of 0.2 A in the Hull cell and between 0.3 to 1.0 A/dm² (2.8 to 9.3 A/ft²) in the beaker.

Sensitivity to immersion deposition was tested by immersing strips of polished brass and bright nickel plated brass into the solution for 10 and 20 sec. The strips were then examined for the presence of any immersion deposits.

The appearance of the plated silver deposit on brass or bright nickel-plated brass panels was evaluated either by visual inspection of the reflection of black text printed on standard white photocopy paper as illustrated in Fig. 1 or by measurement of the reflectivity using a gloss meter.^{**}

Adhesion over copper (brass) and bright nickel was qualitatively evaluated by bending the high current density area of a Hull cell panel back and forth twice at 90° and examining the deformed panel areas for signs of cracking, blistering and/or peeling.

Preparation of cross sections was carried out via standard methods and they were examined by light microscopy.^{***} The microstructural features of the deposited coatings were investigated using a scanning electron microscope.

Vickers microhardness tests were carried out following the ISO/DIS 4516 standard (ISO 1463 resp. ISO 6507, parts 1-3) normal to the coating surface.^{****} The minimum thickness was 20 μm (787 μ-in). Solderability tests were carried out following German standard DIN IEC 68-2-20, parts 2-20. The soldering behavior and contact resistance were investigated at the job shop plater using their internal standard methods. The thioacetamide corrosion test was conducted according to EN ISO 4538:1995 at the plating shop as well.

Results and discussion

Adhesion, immersion behavior and brightness

No immersion deposition, either on brass or on bright nickel-plated brass strips, was observed after immersion in the solution for 10, 20 or even 30 sec. This suggests that the susceptibility to metallic contamination was very low.

The appearance of the silver deposit was very bright and white when deposited over brass. Even over bright nickel we observed a rather bright and white silver deposit. Figure 1 shows the appearance of the two silver coated Hull Cell panels. In order to make the evaluation more concrete and tangible, the reflectivity of the semi-bright silver deposits was measured. The deposit from a typical cyanide solution revealed values of up to 80%. The EAS process yielded comparable reflectivity rates of about 78%.

The silver deposit from the EAS system showed adequate adhesion over brass and even over bright nickel as can be seen in Fig. 2. No blistering or peeling was observed, neither during silver plating nor with the bending test.

** *Mirror TRI-Gloss, Byk-Gardner GmbH, Geretsried, Germany; Byk-Gardner USA, Columbia, MD.*

*** *Zeiss Axiotech, Carl Zeiss, NA, Thornwood, NY.*

**** *Shimadzu HMV-1, Shimadzu Co., Kyoto, Japan.*

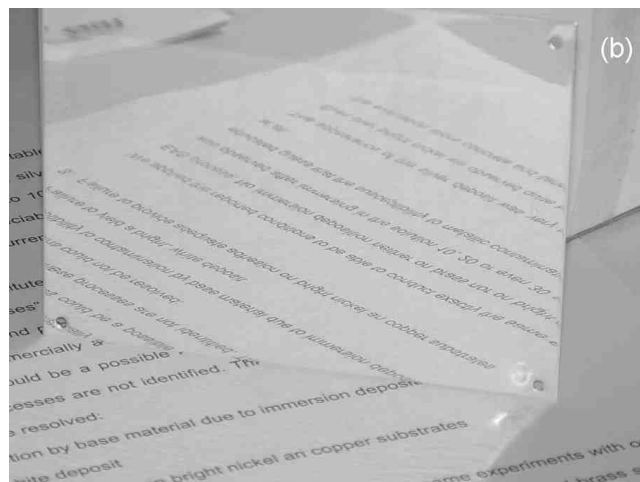
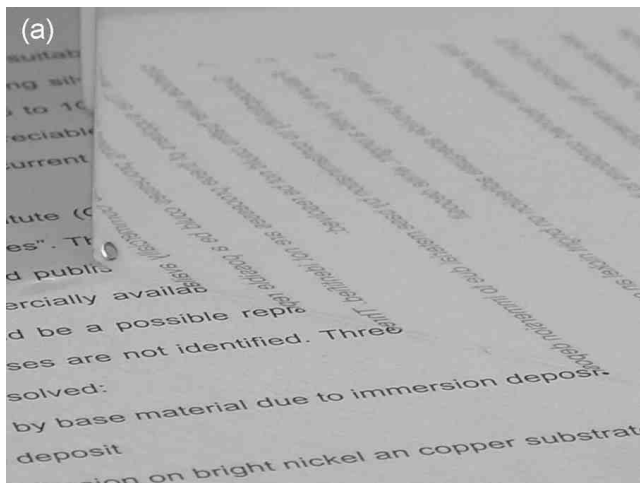


Figure 1—Appearance of EAS silver plated (a) over brass and (b) over bright nickel.

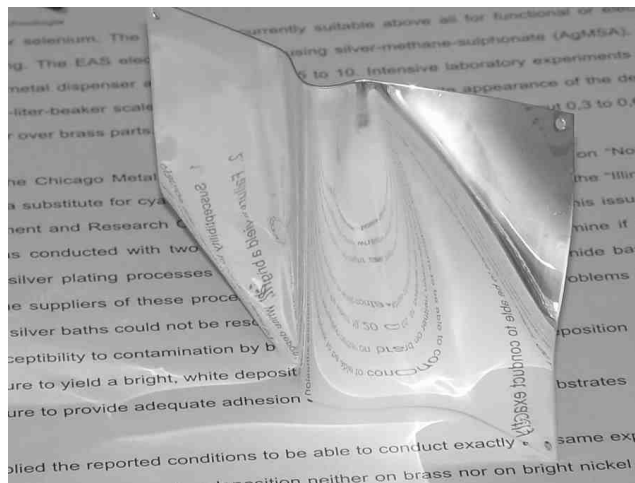


Figure 2—Adhesion test (passed) results for EAS-based silver over bright nickel-plated brass.



Figure 3—Silver-plating of bulk articles with EAS-based silver.

Commercial plating experience

The non-cyanide silver process can be operated in a way that avoids the problems mentioned above. After resolving them, we had the opportunity to run the process in a commercial trial. The trials were performed in a 250-L (66-gal) tank at a job shop electroplater who normally performed cyanide silver plating. This allowed us to compare both processes under similar operating conditions including any plating problems that might arise. Figure 3 illustrates barrel silver-plated articles from the EAS-based process.

Electrolyte properties

Table 1 provides an overview of different silver electrolyte types. The EAS-based system operates in the usual range of silver plating processes with a metal content of 30 g/L (4.0 oz/gal), at a pH of around 9.8. With typical cathode current densities ranging from 0.3 to 0.4 A/dm² (2.8 to 3.7 A/ft²) for barrel plating and up to 1.0 A/dm² (9.3 A/ft²) for rack plating, deposition rates up to 0.6 μm/min (23.6 μ-in/min) are attainable, corresponding to current efficiencies of about 98 to 99%. These values lie within the known range applicable to cyanide baths. In addition, the EAS-based solution makes it possible to carry out silver-plating without pre-silvering over diverse substrate materials such as beryllium copper while still obtaining excellent adhesion.

The alkali-carbonate required for increasing conductivity and throwing power in cyanide electrolytes is not used in the non-

cyanide process. Owing to the absence of cyanide, no carbonate is generated and the elimination of surplus K₂CO₃ or Na₂CO₃ is moot.

The process can be run in normal silver-plating facilities with fine silver recommended as the anode material. Technical application trials under industrial production conditions have been carried out in a commercial electroplating shop. Figure 4 shows a manual system using the EAS-based solution applied to the silver-plating of bulk articles. The EAS-based process provided good throwing power, resulting in excellent coating thickness distribution. Figure 5 illustrates EAS-silver plated brass bolts with an internal hole.

The cross sections of the bolts are shown in Fig. 6. The average coating thickness on the outside was approximately 4 μm (156 μ-in). The mean thickness value on the inside measured approximately 2.5 μm (98 μ-in). Excellent metal distribution is clearly visible. Uniform plating can be obtained even on complex geometries, thus economizing on silver usage.

Coating properties

It almost goes without saying that any alternative process must meet or exceed the properties and performance of conventional commercial cyanide silver plating. As seen in Table 2, the characteristics of silver coatings obtained from the cyanide-free EAS electrolyte are on a par with cyanide silver and in some cases

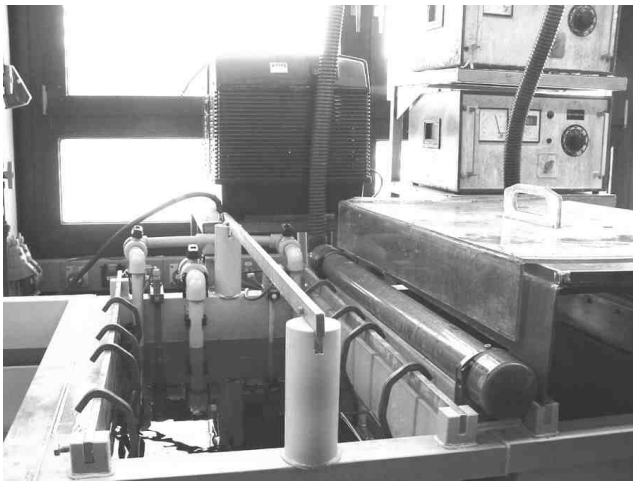


Figure 4—EAS-based production bath installed at a job shop facility.

surpass them. As reported by Dini, *et al.*¹³ and others, silver from a cyanide-free process can offer similar physical and electrical properties despite the slightly yellow appearance of the deposit.

Such parameters as brightness, color, adhesion, solderability and heat resistance [1hr at 250°C (482°F)] correspond to specified values. Contact resistance, of immense importance in electronic applications, lies within the approximate range of 2.5 mΩ.

The thioacetamide test was carried out for detecting corrosion in aggressive media. Compared to cyanide deposits, silver coatings



Figure 5—Silver-plated brass bolts with an internal hole.

obtained from EAS-based solutions show that it took twice as long (*i.e.*, 7.0 versus 3.5 hr) before a yellow tinting was observed. This corrosion behavior may be related to the relatively low sulfur content in the deposit. The standard commercial semi-bright cyanide silver electrolyte yields up to 0.5 wt% sulfur at the deposit surface. No sulfur was detectable on the surface of the silver deposit obtained from the cyanide-free electrolyte. Figure 7 shows the content of sulfur found

by glow discharge mass spectrometry (GDMS) in the silver layer. Only traces of carbon were evident in the near-surface areas of both silver coatings, below 0.05 wt%.

The microhardness measurements of the non-cyanide silver deposits showed values of up to 140_{VHN}, without the use of hardening additives such as antimony or selenium.

The bright plated coatings revealed a compact-grain texture. Figure 8 shows a scanning electron microscope image (SEM) of a silver coating obtained from a standard commercial cyanide

Table 1
Overview of different silver-electrolyte types

	Cyanide Type	Thiosulphate Type	EAS Type
Silver compound	KAg(CN) ₂	Ag ₂ S ₂ O ₃	Ag-EAS
Silver content, g/L (oz/gal)	20 to 40 (2.7 to 5.3)	30 (4.0)	20 to 40 (2.7 to 5.3)
Free cyanide, g/L (oz/gal)	30 to 120 (4.0 to 16.0)	-	-
Temperature, °C (°F)	RT	15 to 30 (59 to 86)	15 to 25 (59 to 77)
pH	>12	9 to 10	9 to 10
Deposition rate, μm/min (μ-in/min)	0.3 to 1.5 (12 to 59)	0.3 to 1.0 (12 to 39)	0.3 to 1.2 (12 to 47)
Current efficiency	98 to 99%	98%	98 to 99%
Current density, A/dm ² (A/ft ²)	0.5 to 2.0 (4.6 to 18.6)	0.5 to 1.5 (4.6 to 13.9)	0.3 to 1.0 (2.8 to 9.3)
Additives	Se, Sb and Organic brightener	-	No Se or Sb; Organic brightener
Anodes	Silver	-	Silver
Application	Technical & decorative	Decorative	Technical & decorative
Application method	Rack & barrel	Rack & barrel	Rack & barrel

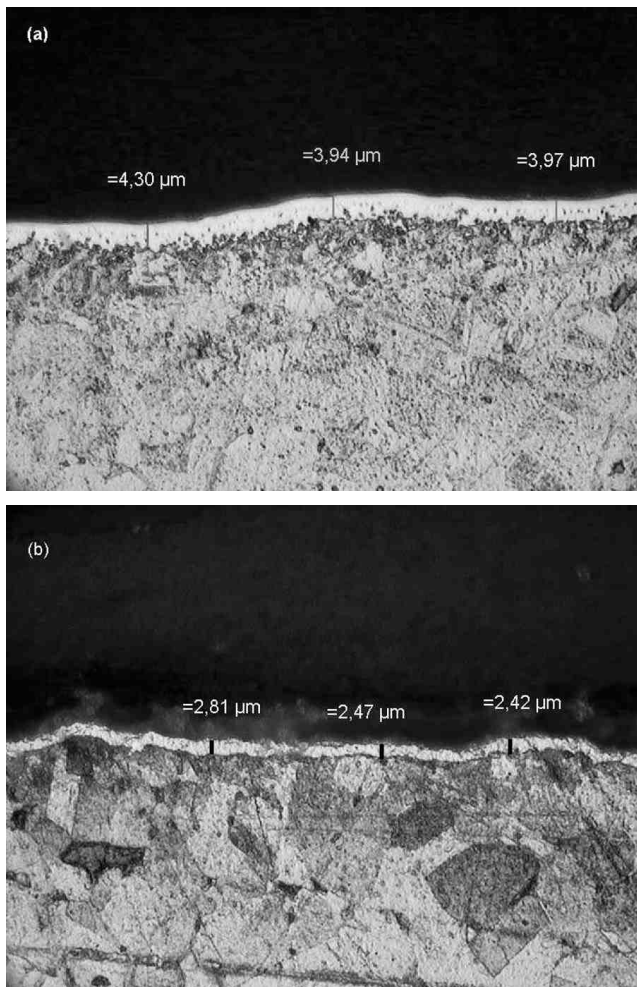


Figure 6—Cross sections of silver-plated bolts: (a) outside and (b) inside coating thickness.

electrolyte. Figure 9 provides a comparative illustration of SEM images of the silver deposits obtained from the cyanide-free bath with and without additives. The grain size of the silver coating obtained from the AgMSA-based, additive-free EAS bath measured up to 5 μm (197 μ-in). Adding the grain-refinement additive reduced the size of the crystallites to well below 1 μm (39.4 μ-in) which in turn led to a distinct increase in the degree of brightness of the silver coating thus obtained.

Conclusions and prospects

A newly developed cyanide-free silver electrolyte, based on albuminate amino acid chemistry, has been tested under standard production conditions. It allows technical silver-plating without the use of cyanide. No pre-silver plating is necessary for coating non-ferrous metal materials. The properties of the coatings deposited from this solution are at least on a par with known characteristics pertaining to cyanide electrolytes. Additional advantages to be gained involve industrial safety and improved waste-water treat-

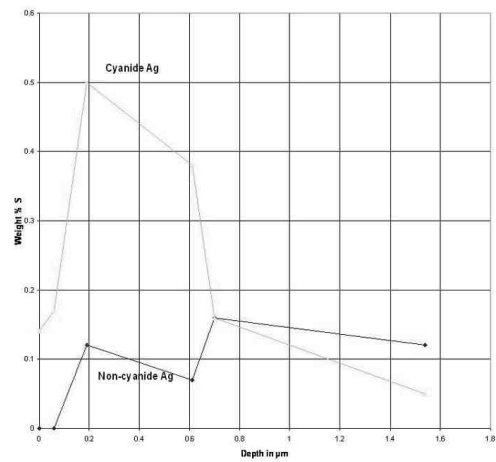


Figure 7—Comparison of depth profile of sulfur content for cyanide-based and EAS-based silver processes.

Table 2
Comparison of coating properties

	Cyanide Type	Thiosulfate Type	EAS Type
Silver percentage	98 to 99.9%	-	98 to 99.9%
Alloy component	None	-	None
Hardness ($H_{VHN10'25}$)	100 to 120	150	100 to 140
Contact resistance	2.5 mΩ	-	2.5 mΩ
Corrosion resistance*	~ 3.5 hr	-	Up to 7 hr
Solderability	Good	-	Good
Color	White	White	White
Brightness	Bright	Bright	Bright

* Thioacetamide test: Time to yellow tint

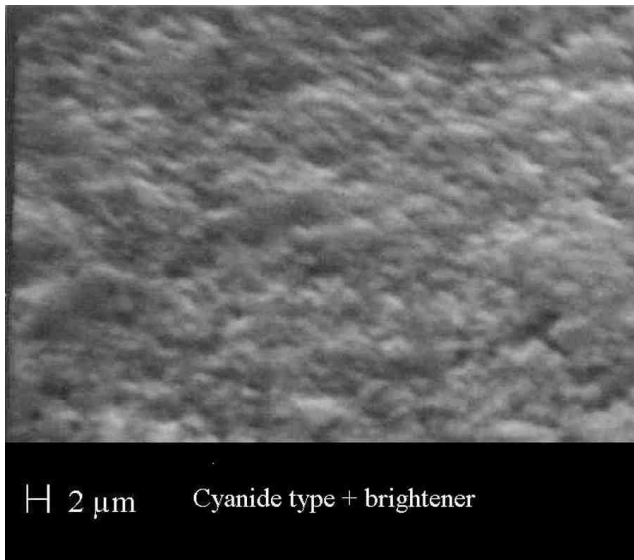


Figure 8—SEM image showing the surface of a silver coating obtained from a cyanide bath.

ment protocols. The costs of the overall process are competitive with cyanide.

Currently this non-cyanide solution makes it possible to conduct silver plating in rack and barrel applications with no limitations as to process parameters or coating characteristics. Ongoing research shows that distinctly higher current densities can be applied by increasing electrolyte agitation. At the present time, deposition rates of up to 10 $\mu\text{m}/\text{min}$ at 20 A/dm^2 (394 $\mu\text{-in}/\text{min}$ at 186 A/ft^2) are attainable. This knowledge, already backed to some extent by practical experience, raises hopes that the process may be applied to continuous line facilities under high-speed conditions.

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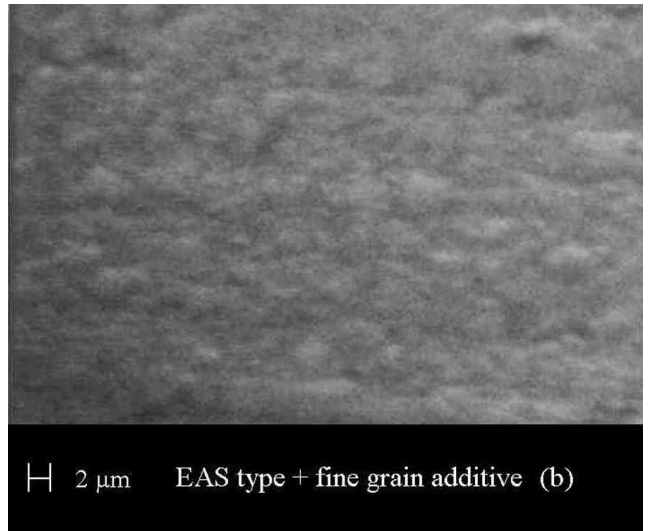
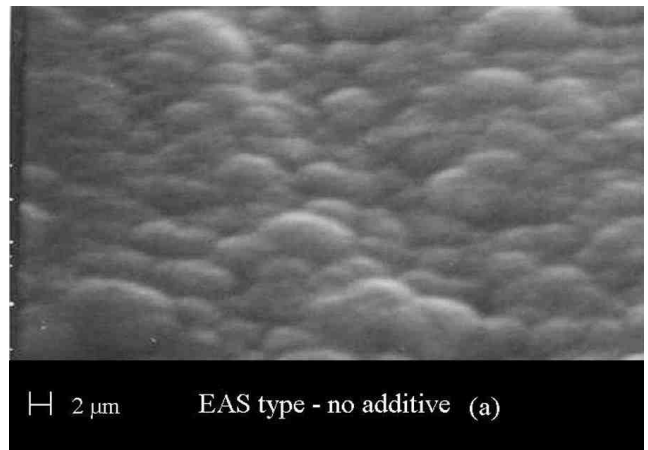


Figure 9—SEM images showing the effect of a grain refiner on the surface roughness and grain size of the EAS-based silver coating: (a) without the additive, (b) with the additive.

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