Internal Stress of Electroless Nickel Deposits

by David E. Crotty, Ph.D. & Nicole Micyus*
MacDermid Inc., 29111 Milford Road, New Hudson, MI USA

The internal stress of electroless nickel deposits has long been known to be a very important physical property of the deposits. In some cases the stress can be the most important factor to determine the suitability of a deposit for a specific application. A wide range of new processes have been introduced into the market to meet new regulatory requirements. This paper discusses the results of internal stress studies on some of these processes and provides comparisons with deposits prepared by traditional electroless nickel processes.

Keywords: *Internal stress measurement, internal stress properties, electroless nickel, pH control*

Introduction

Electroless plated nickel/phosphorus deposits are known to develop an intrinsic property called internal stress. This property is an important aspect of the deposit that affects adhesion on some substrates and may have an effect on wear properties. The property is discussed briefly by Riedel[1] and Malloy and Hajdu.[2] Dini[3] also discusses the causes and effects of internal stress in electroless deposits.

This property was studied most extensively for electrolytic deposits such as sulfamate nickel[4] because of the importance for certain applications and is usually measured using the Brenner-Senderoff spiral contractometer.[5] The spiral winds or unwinds depending on the stress and the amount of winding can be accurately measured.

The spiral contractometer is somewhat difficult to use, especially at the high operating temperatures used for electroless nickel/phosphorus processes. Recently another method has been described[6] that was invented by Bartlett[7] in 1969. This method uses a steel strip held in a block so that only one face is plated. The stress from the deposit on one side of the strip bends the strip and the amount of bend can be measured with a micrometer.

While the internal stress is a very important property of electroless nickel deposits, the measurements are seldom performed due to the difficulty. The stress strip method is fairly easy to perform and is applicable for use with electroless nickel. This paper investigates the internal stress of several different types of electroless nickel deposits and in some cases compares the results obtained from the spiral contractometer method and the Bartlett stress strip method.

This paper will also compare conventional processes with processes that meet the original requirements of the European Union ELV (end of life vehicle)[8] mandate in which intentional addition of materials like lead and cadmium were forbidden. That requirement was modified in September 2005 to allow additions if under the specified content. The NSF 51[9] still forbids intentional use of these and other materials.

Equipment and methods

The spiral contractometer is available from at least two vendors.[10] The items needed for the Bartlett stress strip method are not readily available. However, the items, made of polypropylene for high temperature work, were provided by Palm International.[11] The stress strips were prepared and plated as described in the previous paper.[6]

Figure 1 shows the spiral contractometer including two types of clamps used to hold the spiral to the fixture. The plastic clamp uses Allen screws to clamp the spiral down. The screws have to be tightened fairly well to keep the spiral from slipping at high temperature and the tightening of the screw eventually strips the threads in the plastic and thus allows the spiral to slip. The stainless steel clamp, also in the picture, is the more effective of the two devices. However, the screw that holds the clamp down becomes plated and can be difficult to unscrew with a mil (25 μm) of electroless nickel deposit in the threads. All spiral contractometer work discussed here was conducted using stainless steel spirals coated on the inside with PTFE, and the stainless steel clamps.

Figure 2 shows the equipment for the Bartlett method.[6] This consists of a measuring block in which the strip's bend is measured before and after plating, and the plating block. The steel strip slips into the plating block so that only one side is exposed for plating.

In both cases, the deposit is plated until there is about 1 mil (25 μm) of plating thickness. Also, it is customary for tensile internal stress to be expressed as a positive number (clockwise dial rotation) and compressive stress to be expressed as a negative number (counter clockwise dial rotation).

Background

Typical internal stress results[12] for the three basic types of electroless nickel/phosphorus, high phosphorus (11 wt% P), high-medium phosphorus (9 wt% P), and low-medium phosphorus (4 wt% P) are shown in Figure 3. These processes are conventional processes.[13]

In general, high phosphorus deposits are compressive when the plating process solution is new. The internal stress may creep up a bit as the process solution ages but will turn upward at some point above four metal turnovers (MTO). Usually the stress becomes tensile and the process solution is no longer usable for many applications.

The medium phosphorus deposits will be tensile when the process solution is new. The deposits that are 6 to 9 wt% P will tend to show slightly higher tensile internal stress as the process solution ages. Deposits with lower phosphorus content, about 3 to 5 wt%, may show a tendency for the internal stress to drop to lower tensile values as the process solution ages. However, these are general trends. Specific process solutions may show different behavior as will be seen in the results section.

* Corresponding author:
Nicole Micyus
MacDermid, Inc.
29111 Milford Rd.
New Hudson, MI 48165
Phone: (248) 437-8161; ext 138
E-mail: NMicyus@macdermid.com

Figure 1—Spiral contractometer equipment.

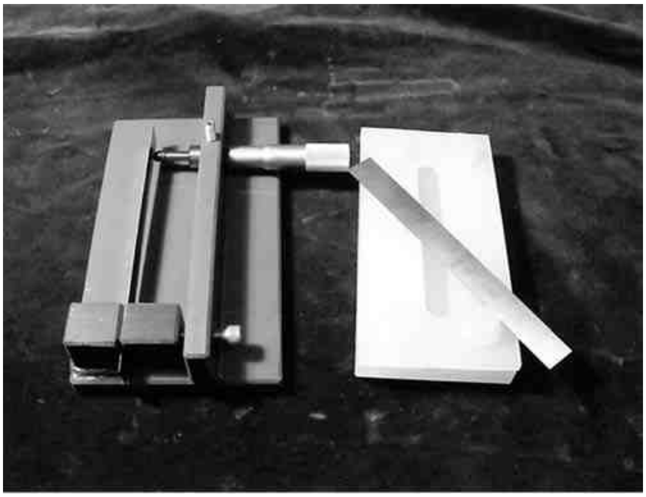

Figure 2—Bartlett stress strip equipment.

Results

During the development of the ELV processes close attention has been paid to the internal stress as the process solution ages. Table 1 shows the results of some of these studies.

The conventional processes typically exhibit the behavior described above. The recent retesting, shown in Table 1, of the conventional medium phosphorus process C7% correlates well with previous experience. This retest was conducted using the spiral contractometer method with a stainless steel spiral and a sulfamate nickel strike.

The three ELV processes, ELV5%, ELV8% and ELV11%, are designed to use a mixture of metallic and non-metallic stabilizers and brighteners to replace the conventional lead and cadmium. The ELV11% internal stress results, obtained using the spiral contractometer, show behavior typical of a high phosphorus processes. However, the low-medium phosphorus ELV5% and medium phosphorus ELV8% were designed with stress control in mind and the internal stress remains fairly low during the life of the process solutions with the internal stress actually dropping a bit as the bath ages. Table 1 presents the internal stress data from recent tests.

Table 1 also provides internal stress data collected recently for a group of processes that are designed to use non-metallic stabilizers and brighteners. The testing of this series was used to compare the results obtained using the two internal stress methods. The low-medium phosphorus process, ELVnm5%, shows behavior similar to the ELV8% process discussed above. The internal stress remains low during the process solution life and drops as the bath ages. The stress values obtained from the two methods, spiral contractometer and Bartlett stress strips, are very similar. This encouraged us to use the Bartlett method for other investigations.

The testing of the next process, ELVnm9% was truncated a bit in that the Bartlett method was used to study the process solution through its life, but the spiral contractometer was used to test only the fresh process solution and then at six MTOs. While the numbers are different for this comparison, they are not really out of range from the expected. The ELVnm9% process exhibits slightly higher tensile internal stress than most processes.

The high phosphorus process, ELVnm11%, follows typical behavior for a high phosphorus process and remains compressive to about 4.5 MTOs.

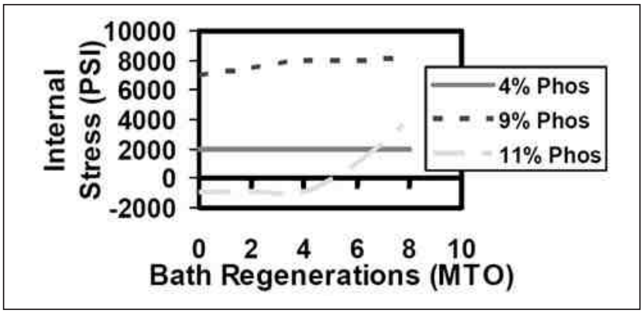

Figure 3—Typical internal stress values.

Caustic soda vs. ammonia for pH control

The use of ammonium hydroxide for pH control is probably the most commonly used method. The ammonium hydroxide, when diluted to about 30% of full strength, mixes easily into the hot process solutions. However, workers object to the strong and dangerous odor and in some localities it is much more expensive to dispose of spent electroless nickel solutions that contain ammonia. Potassium carbonate has been used extensively in the past with some success. However that method reduces the life of the process solution because the mixed salt sodium potassium sulfate is much less soluble than other sulfate salts and crystallizes from the process solution after about four to five MTO. Also, the evolution of carbon dioxide gas on addition of the potassium carbonate solution can be hazardous if the solution is added too quickly. These issues have prompted many EN platers to use dilute sodium hydroxide for pH control.

The use of sodium hydroxide has its problems too. Even sodium hydroxide diluted to 10% will cause nickel to precipitate in a gelatinous mass when added to the hot process tank. Some methods have been developed[14] to cool the plating bath, add the sodium hydroxide and then re-introduce this solution to the plating tank. Also, some EN platers have learned to add diluted 10% sodium hydroxide into the filtration system so that it mixes with the process solution quickly enough to avoid the nickel precipitation.

Table 1
Internal stress measurements of conventional and ELV process deposits measured comparing spiral contractometer vs. Bartlett stress strips

Process	0 MTO PSI/MPa	2 MTO PSI/MPa	3 MTO PSI/MPa	4 MTO PSI/MPa	5 MTO PSI/MPa	6 MTO PSI/MPa
C11%(a)	-9,436 -65.0	-7,200 -49.7	-9,320 -64.2	-8,650 -59.7		
C7% (a)	5000 34.5	3,900 26.9		5,000 34.5	7,000 48.3	10,000 69.0
ELVnm11% (a)	-1070 -7.4	-850 -5.9	-2900 -20.0	-3640 -25.1		
ELVnm11% (b)	-737 -5.1	-1080 -7.4	-1280 -8.8	-2330 -16.1		
ELVnm9% (a)	9,400 64.8					6,900 47.6
ELVnm9% (b)	6,920 47.7	12,300 84.8		15,000 103.4		13,500 93.1
ELVnm5% (a)	4,450 30.7	3,800 26.2	1,500 10.3	-2,000 -13.8		~0 ~0
ELVnm5% (b)	4,050 28.0	6,800 46.9	3,570 24.6	-600 -4.1		~0 ~0
ELV11%(a)	-1,100 -7.6	-700 -4.8	-1,600 -11.0	1,500 10.3	5,900 40.9	6,700 46.2
ELV8% (a)	8,800 60.7	7,100 49.0		5,800 40.0	5,400 37.2	5,400 37.2
ELV5% (a)	1,110 7.7	-3,700 -25.5	-2,700 -18.6	-4,000 -27.6	-3,900 -26.8	-4,500 -31.0

Notes:
1. (a) Spiral Contractometer, Stainless Steel, (b) Bartlett Stress Strips
2. ELVnm processes non-metal stabilized; ELV processes metal/nonmetal stabilized.
3. C processes are "conventional."
4. Tensile Stress-Positive; Compressive Stress-Negative.
5. All processes pH controlled with ammonia.

The issue that opened our eyes occurred when we took the experimental ELVnm9% process solution to a shop that had long used a conventional high-medium phosphorus process that we will call C9%. This shop controlled the pH by feeding diluted NaOH solution into the filtration system. The stress data for the conventional process and the ELV process was very high compared with known data for ammonia-controlled processes as shown in Table 2. The internal stress measured for these systems is surprising. We began to look closely at processes and how they respond to pH control.

Table 2 shows typical internal stress behavior expected for medium phosphorus processes C7% and ELVnm9% with ammonium hydroxide control. Also shown are the stress results obtained for the C9% and the ELVnm9% processes from the process tanks at this shop as the two process solutions aged. The stress rises rather dramatically. However, there was no adhesion loss on the hardened parts plated in these tanks and the parts performed well in service.

We investigated this issue and were able to reproduce the rise in tensile internal stress with dilute NaOH pH control in the laboratory. Also, we found that if the aged (eight MTOs) solutions were used with ammonium hydroxide adjustment, the internal stress decreased. For these tests 1.0 L of the C9% 8-MTO solution was adjusted with ammonium hydroxide and the process components, and plated with a ½ Hull cell panel for 30 min. The internal stress dropped from 455 to about 240 MPa (66,000 to about 35,000 lb/in^2). Once the solution was adjusted again using ammonium hydroxide and plated again for 30 minutes the stress dropped to 159 MPa (23,000 lb/in^2). Obviously sodium hydroxide is capable of this strong influence on the internal stress and ammonium hydroxide has the ability to keep the stress lower.

As a further investigation we have been developing a NaOH MIX that allows the operator to add the alkaline solution directly to the plating bath without causing the nickel to precipitate. The test process for this investigation is the ELVnm5% process that normally shows low tensile internal stress when controlled with ammonium hydroxide. Table 2 shows that the internal stress of the ELVnm5% process drops from tensile to compressive stress when the NaOH MIX is used. This interesting result suggests that the composition of the plating bath has an influence on how the sodium hydroxide will affect the internal stress as a bath ages. It is

Table 2
Comparison of conventional and ELV electroless nickel internal stress: pH control with diluted NaOH vs ammonia and pH control with potassium carbonate

Process pH control	0 MTO PSI/MPa	1 MTO PSI/MPa	2 MTO PSI/MPa	3 MTO PSI/MPa	4 MTO PSI/MPa	5 MTO PSI/MPa	6 MTO PSI/MPa	8 MTO PSI/MPa
C7% ammonia (a)	5,000 34.5		3,900 26.9		5,000 34.5		10,000 69.0	
C9% NaOH (b)(c)	5,790 39.9		17,200 118.6		18,000 124.1			66,500 458.6
ELVnm9% ammonia (b)	9,000 62.1		12,300 84.8		15,000 103.4		13,500 93.1	
ELVnm9% w/NaOH (b)	9,290 64.1		22,730 156.7		35,000 241.3		36,600 252.4	54,700 377.2
ELV8% w/K2CO3(a)	9,000 62.1	15,200 104.8	11,100 76.5	10,400 71.7	6,000 41.4	4,900 33.8		
ELVnm5%(a) NaOHMIX(c)	9500 65.5		1890 13.0	-4876 -33.6			-4962 34.2	
ELVnm5%(b) NaOHMIX(c)	8345 57.5		5400 37.2	-2250 -15.5			-3915 27.0	

Notes:
1. (a) Spiral Contractometer, Stainless Steel, (b) Bartlett Stress Strips, (c) operated at 3 g/L nickel.
2. ELVnm processes non-metal stabilized; ELV processes metal/nonmetal stabilized.
3. C processes are "conventional."
4. Tensile Stress-Positive; Compressive Stress-Negative.
5. All processes pH controlled with ammonia.

likely that this approach will find considerable interest in the field. However, this area needs further research.

Potassium carbonate for pH control

Potassium carbonate is used frequently to produce self pH regulating processes that do not contain ammonia. The potassium carbonate is more useful than sodium carbonate, for example, because it is the much more soluble of the two so that enough can be formulated into a concentrated replenishment additive. Table 2 shows (Fig. 4) the results of preparing the ELV8% process as the potassium carbonate self pH adjusting process (See Table 1 for the same process controlled with ammonia). The unexpected result is that the internal stress rises quickly at one MTO to 104.8 MPa (15,200 lb/in^2) but slowly drops as the process solution ages. The pH value is well known to affect strongly the internal stress. However, in this case the process maintains at about pH 5.0 as a young process solution and drops only to about 4.9 at five MTOs. The process used for this test series shows a natural tendency for lower internal stress as the process solution ages. Thus, it is possible that this tendency has a strong effect on the behavior shown here.

Finally, a test was run using the same chemistry in which the process was maintained using ammonia for one MTO. The internal stress at that point was 49.7 MPa (7,200 lb/in^2), essentially the same as a fresh bath in Fig. 4. The process was continued but ammonium hydroxide was used to maintain the pH to two MTOs. The internal stress was 51.7 MPa (7,500 lb/in^2). As with the discussion of NaOH control, an amount of ammonia has a strong effect in modifying the effect of potassium carbonate on the internal stress.

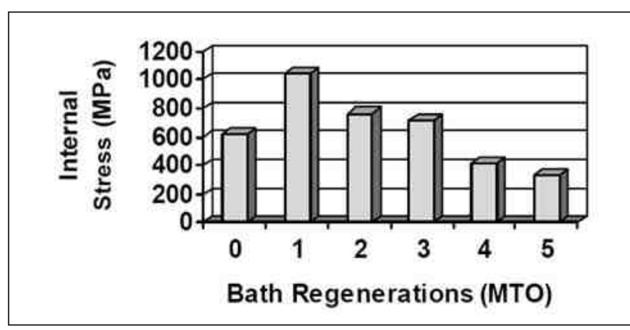

Figure 4—Carbonate pH control.

Comparisons of spiral contractometer vs. Bartlett methods

Tables 1 and 2 contain two direct comparisons of the two internal stress measurements. Table 1 contains the data for the ELVnm11% process life test. In that test series the stress was measured using both the spiral contractometer and the Bartlett method. Table 2 contains a life test for the ELVnm5% process operated at 3.0 g/L nickel ions and 20 g/L of sodium hypophosphite. During that life test the two methods were also used to measure the internal stress. Figure 5 illustrates the method comparison when the ELVnm11% process was tested. Figure 6 shows the data for the ELVnm5% process operated at 3.0 g/L nickel ions. The process illustrated by Fig. 6 is a newly popular "low metal operation" variation[15] in which the process solution is used at 3.0 g/L of nickel and 20 to 25 g/L of sodium hypophosphite. This method saves some operating cost and lowers wastes due to drag out.

Figures 5 and 6 show that there are some differences in the results of the two methods. Some of the differences may result from the difficulties in operating the spiral at high temperature. But there is also the issue of thermal expansion changes as the basis metal and the plated layer cool. The last issue will be investigated later.

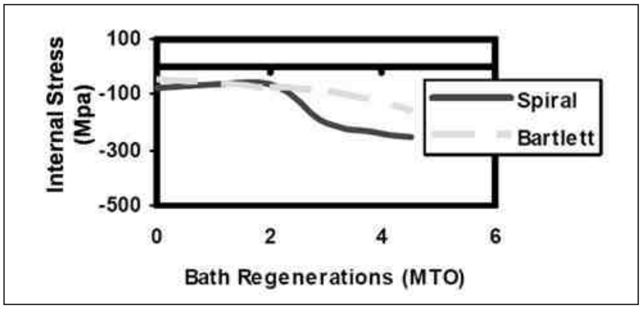

Figure 5—Internal stress vs. number of metal turnovers - 11% phosphorus process.

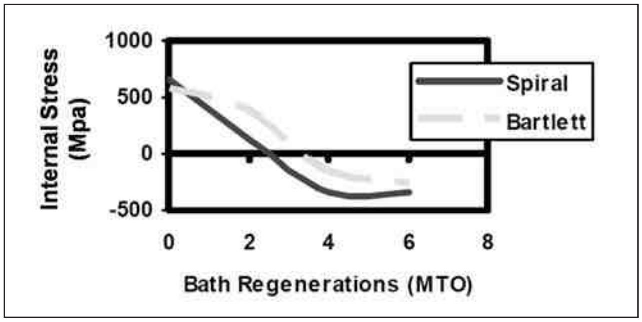

Figure 6—Internal stress vs. number of metal turnovers - 5% phosphorus process.

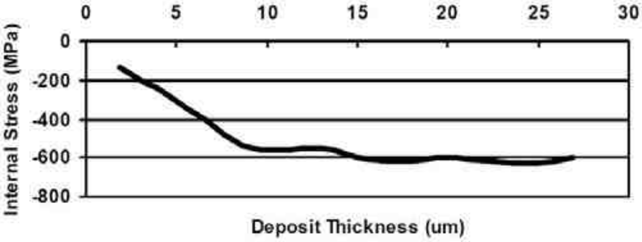

Figure 7—Internal stress vs. deposit thickness.

The effect of deposit thickness

The internal stress of a deposit is probably relatively constant as deposit thickness builds. However, the measurement of this property is somewhat dependent on the substrate. Figure 7 illustrates data collected using a stainless steel spiral. The stress was measured at numerous points as the deposit thickness of a C11% deposit grew. The apparent internal stress measured builds as the deposit builds. The calculation for internal stress contains terms for thickness of the deposit and substrate properties, and ideally this should compensate. However, it is well known that this is not the case. The deposit really needs to be above 12 μm (0.5 mil) before the true internal stress is observed as borne out by the data.

Summary

- Two methods were compared to measure the internal stress of electroplated and electroless plated deposits. The spiral contractometer method is well known and has been demonstrated to be reliable and accurate. The Bartlett method is less well known but has some interesting properties, including that almost any substrate can be tested. The spirals are only available in stainless steel and aluminum.
- Studies described here show that the two methods provided similar results, although there are expected to be some differences related to thermal expansion as metals cool.
- The internal stress behaviors of a number of electroless nickel processes were compared. For the most part, the newer ELV compliant (lead- and cadmium-free) deposits exhibited internal stress behavior that was similar to comparable conventional deposits. However, in some cases the ELV compliant processes were sufficiently different that the internal stress behavior differed from the conventional processes.
- Internal stress behavior was discussed both for processes that use a mix of metallic and non-metallic materials for stabilization and brightness, and for processes that use only non-metallic materials for these purposes. Again, similarities and differences can be seen between these processes, depending on the composition of the process solutions.
- The effect of sodium hydroxide pH control on the internal stress was investigated. It appears that the use of this material may have had a strong effect on the internal stress. However, the use of a formulated NaOH mixture for pH control appears to have had a very different effect on the stress behavior.
- Several examples presented in this discussion were deposits plated from the low metal operation method.
- The work presented here is a preliminary look at the internal stress behavior of these new classes of electroless nickel processes. Investigations continue and further results will be reported later.

Acknowledgements

The authors would like to acknowledge the support of this work by MacDermid, Inc. The authors also recognize some work reported here by Gian Lanza, a research chemist now retired, at MacDermid, Inc.

References

1. W. Riedel, *Electroless Nickel Plating*, ASM International, Materials Park, Ohio, 1991; p. 109.
2. G.O. Mallory & J.B. Hajdu, eds., *Electroless Plating: Fundamentals & Applications*, National Association for Surface Finishing, Washington, DC, 1990; p. 121.
3. J.W. Dini, *Electrodeposition: The Materials Science of Coatings and Substrates*, Noyes Publications, Park Ridge, NJ, 1993.
4. J.L. Marti, *Plating*, **53** (1), 61 (1966).
5. A. Brenner & S. Senderoff, *Proc. Amer. Electroplaters Soc.*, **35**, 53 (1948) and ASTM B636-84(2006)e1 "Standard Test Method for Measurement of Internal Stress of Plated Metallic Coatings with the Spiral Contractometer," ASTM International, West Conshohocken, PA.
6. D.E. Crotty, *Plating & Surface Finishing*, **91** (10), 56 (2004).
7. B.C. Bartlett, L. Cann & J.L. Hayward, *Plating*, **56** (2), 168 (1969).
8. End of Life Vehicle (ELV) Directive 2000/53/EC Annex II September 2005.
9. NSF/ANSI 51-2005 Food Equipment Materials, NSF International, Ann Arbor, MI (2005).
10. Kameras Instruments, P.O. Box 399, Garret Park, MD and Larry King, 13708 250th St., Rosedale, NY.
11. Palm International, 1717 Hennessy Dr., LaVergne, TN.
12. D.E. Crotty & C. Steinecker, *OxyChem EN News*, **8** (2), 2 (1991/1992).
13. D.E. Crotty, *J. App. Surf. Fin.*, **1** (1), 56 (2006).
14. B.H. Morcos, U.S. Patent 6,500,482 (2002).
15. M. Barnstead, *Products Finishing*, **7** (6), 40 (March 2007).

About the Authors

David Crotty obtained B.S. and M.S. degrees in chemistry at Xavier University in Cincinnati and a Ph.D. in chemistry at Wayne State University in Detroit. He has worked in the metal finishing industry since 1980 as a research and development chemist and has recently retired. The areas of research have included electroless nickel plating, zinc plating, zinc alloy plating, tin plating and associated processes. He will continue as editor and author, and expects to teach math and chemistry as well as do some consulting.

Nicole Micyus is a R&D associate chemist for electroless nickel processes for MacDermid, Inc. Nicole obtained a B.S. in Environmental Chemistry from GMI Engineering & Management Institute in 2002 and a M.S. in Chemistry from Oakland University in 2005.