Electrocomponent Science and Technology, 1981, Vol. 8, pp. 159–165
0305-3091/81/0804-0159 $06.50/0

POSSIBILITIES FOR AIR FIREABLE BASE METAL CONDUCTORS

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This paper discusses the status of thick conductive films formed by firing in air. The metals under study include nickel, chromium, aluminum and copper. The properties of the films are presented for firing temperatures ranging from 580 to 850 degrees C. Compatibility with various dielectrics and glasses have been studied. Multilayer wiring seems promising. Potential uses on porcelain enamelled steel, window glass and alumina substrates seem feasible.

Initial studies have been made of compatibility with thick film ruthenium-based resistors. Some preliminary information on termination resistance and other properties observed in such combinations is presented.

Possible applications in gas discharge displays for cathodes and conductor runs are discussed. Potential uses may include economical ground planes, solar cell electrodes, varistor and thermistor terminations, and resistance thermometers.

1. INTRODUCTION

Everyone is aware of the upward price movements of precious metals during the past few years. These price increases have accelerated sharply, especially within the last 2 years. This has resulted in intensive pressures being applied upon users and suppliers to replace these noble metals with lower cost alternatives. Possibilities being studied include process changes, product redesign or replacement by base metals. Additionally, attempts are being made to reduce the amounts of precious metals used where they cannot be totally eliminated.

Silver, gold and the platinum group metals have extraordinary chemical and physical properties. Their reliability, durability and resistance to corrosion, over a wide temperature range, are outstanding. This has contributed to the ease in joining, contacting and wire bonding to them. Most noble metals form ohmic contacts readily and tend to retain such ohmic behavior under severe humidity, high electrical loading, and during processing to almost 1000°C.

Many of these characteristics are not exhibited by the large number of other metals we know. Oxidation (often at room temperature), corrosion, attack by water and other chemical reagents, occurs far more readily with iron, nickel, aluminum, copper, etc.

In the case of thick film compositions, heating such base metal powders mixed with glasses to elevated temperatures in air will usually hopelessly oxidize these metals and cause them to react with the glasses and fluxes present. They will also exhibit erratic contact and joining behavior.

Thus, the early cermet work on base metal conductive cermets was limited to hydrogen (reducing), and nitrogen (inert) atmospheres. Good as-fired properties for copper and nickel have been obtained in such atmospheres, and compatible dielectrics are also available. Nitrogen fireable resistors, on the other hand, have decided performance and stability shortcomings. Much more improvement work is required before such resistors can be reliably and widely used in the thick film hybrid electronics field.

The ideal situation would be to be able to fire inexpensive conductors in air, and retain the compatible use of most of the other materials and processes currently employed. Air-fireable ruthenium-based resistors have not increased in price significantly for many years. Many variations with good properties are readily available for firing at various temperatures between 600°C to 1000°C. The same good economical supply situation is true for dielectrics and glazes. Thus, the major need is for reducing the amounts or percentages of Au, Ag, Pt and Pd used in hybrid circuits. Ideally, this should be accomplished by means of air-fireable, lower cost conductors. Part of this objective has been achieved by switching from gold and platinum to high silver content Pd/Ag conductors. However, this paper will discuss some of our efforts in utilizing copper, nickel, aluminum and chromium in air-firing compositions.

A large number of metal powder preparations have been made with varying degrees of success in passivation for high temperature exposure. The availability of good thick film resistors and dielectrics for use in the 580–650°C range has made it feasible to consider several metal conductors including copper, aluminum, chromium and nickel. These have been formulated into developmental conductor compositions, and their firing and other characteristics are presented below:

2. EXPERIMENTAL RESULTS

2.1. Substrate Effects

The four base metal conductors were fired on soda-lime glass, porcelain enamelled steel, 96% alumina, and single crystal silicon wafer substrates. Table I lists the resistivities obtained when fired at 625°C in a 45 minute firing cycle with 10 minutes at peak temperature. The aluminum and chromium gave their lowest resistivities on silicon. On the other hand, the Cu and Ni are lowest on glass and enamelled steel substrates with this firing cycle.

2.2. Effects of Firing Temperature

Figure 1 shows the variation in sheet resistivity as a function of firing temperature on 96% alumina substrates. Belt furnace firing cycles of 45 minutes with 10 minutes at peak temperature have been used.

Nickel, #2554, dropped in resistivity from 70 to 35 milliohms per square (mohms/sq.) as the peak temperature was increased from about 580°C to 930°C.

Aluminum, #2590, started with a higher resistivity of 250 mohms/sq. at 580°C. This dropped sharply to 15 mohms/sq. by about 700°C. Beyond that temperature, resistivity climbed rapidly reaching about 1 ohm/sq. at 930°C. Upon physical examination, tiny molten droplets of aluminum could be seen on the substrates for firing temperatures significantly above

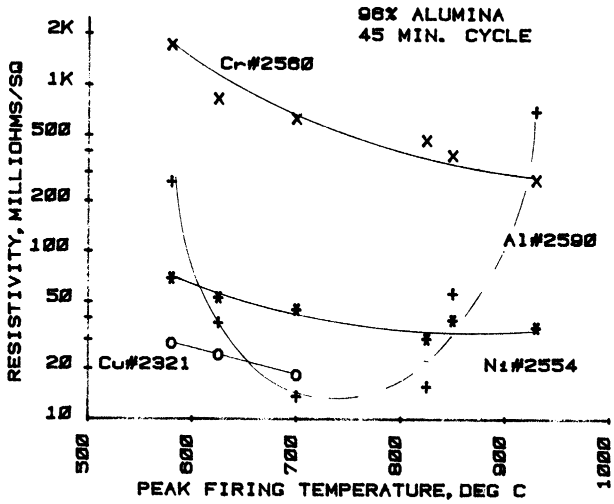


FIGURE 1 Resistivity *vs.* firing temperature.

660°C (the melting point of aluminum.) The aluminum should not be fired in excess of 650–700°C for most applications.

Copper, #2321, varies in resistivity from 28 to 18 mohms/sq. between 580 and 700°C firing. Above 700°C, increasingly severe oxidation is noticeable. Thus, the copper should not be used at the higher temperatures.

Chromium, #2560, exhibits a far higher resistivity than the other three conductors. As temperatures increase from 580 to 930°C, its resistivity will decrease from about 1 ohm/sq. to 300 mohms/sq.

The fired samples of Ni and Cr showed no noticeable signs of oxidation in their physical appearance.

2.3. Effect of Firing Time

Figure 2 presents the data obtained at a constant peak firing temperature of 580°C. The substrate is a soda-lime glass. Belt speed was varied to give total firing times ranging from 25 to 140 minutes.

TABLE I
The effect of various substrates on resistivity (milliohm/square). Peak firing temperature −625°C; cycle time −45 minutes.

	Conductor			
Substrate	Al #2590	Cr #2560	Cu #2321	Ni #2554
Soda–lime glass	37.5	766	15.2	46.2
Porcelain enamelled steel	125.0	646	14.4	45.0
96% Al_2O_3	37.8	829	23.9	53.2
Silicon wafer	11.2	430	24.5	59.0

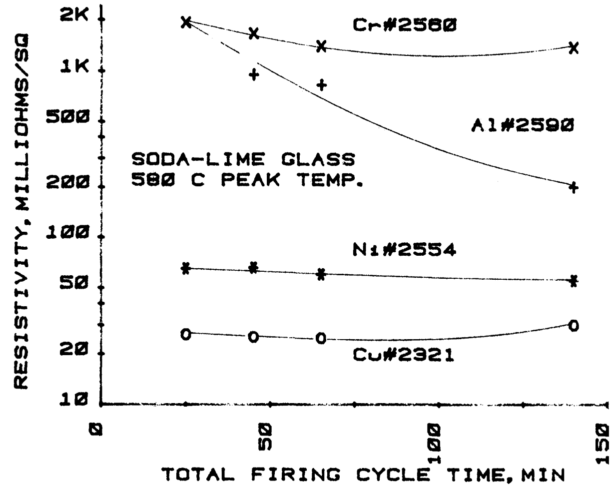


FIGURE 2 Resistivity *vs*. firing cycle time.

Interestingly, both the nickel and copper resistivities seem fairly independent of time at this temperature. Cr shows a moderate drop in resistivity with increasing time. On the other hand, the Al drops more than 1 decade as the time at peak increases over 5 fold. It is obvious that insufficient densification and sintering occur at 580°C for aluminum. By comparing Figures 1 and 2, the aluminum would achieve much better conductivity more quickly, if the firing temperature is raised to the 650–700 region.

2.4. *Multiple Refiring Effects*

Figure 3 shows the effects of refiring these conductors for up to 10 firing cycles. The peak temperature used is 625°C on 96% alumina substrates. The Ni and Cr conductors are apparently stable and show slightly improved conductivity after 10 refiring cycles. However, the Cu and Al are only able to withstand 2 or 3 refires at these conditions before undergoing rapid oxidation. Copper in particular became non-conductive after 5 refires. The aluminum resistivity continues to rise with each refire, but has not completely "run away" even after 10 firings.

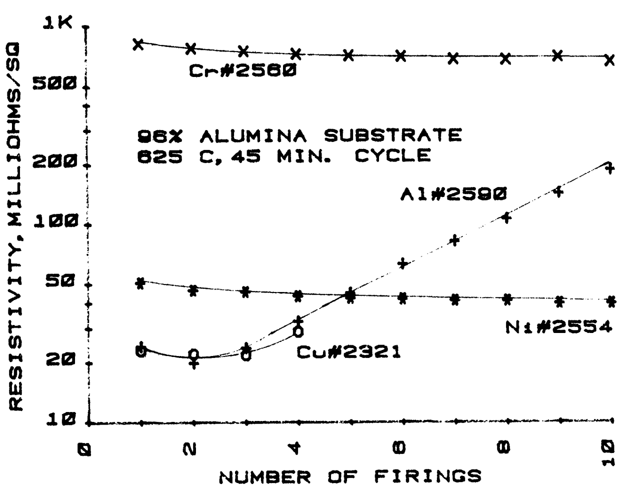


FIGURE 3 Resistivity *vs*. number of refines.

2.5. *Dielectric Compatibility*

Simple crossover and capacitor test patterns have been made using black dielectric #M-4023B. Each of the 4 conductors tested was printed as the bottom electrode and dried. Two layers of the dielectric were then printed and dried. After the top electrode of the same metal was printed, the four layers were all cofired at 580°C. Table II lists the results.

The Ni, Cr and Cu all give satisfactory low picofarad capacitance. The Al gives no measurable capacitance, indicating chemical incompatibility. Application of Ni conductors with #M-4023B in multilayer circuits used in DC gas discharge displays is feasible. Several other nickel variations are available for study in applications such as cathodes, and glass seal feed-through conductors.

Several other thick film multilayer dielectrics (including ESL #M-4030) are under study for use with these conductors at different temperatures. ESL silvers #590 and #595 may also be used as the top conductor layer in combination with a 2, 3, or 4 level Ni multiconductor structure, whenever silver's unique properties are needed. This allows significant reduction of the amount of silver used in a multilayer and avoids dangers of shorting through layers. We have been successful in preparing Ni, Cu and Cr simple multilayers, and also capacitor patterns using #M-4030 dielectric fired at 625°C.

TABLE II
Compatibility with #M-4023B dielectric. All cofired at 580°C for 45 min. cycle, dried between each layer

	Capacitor size 5 mm × 5 mm		Capacitor size 2 mm × 2 mm	
	K	D.F.(%)	K	D.F.(%)
Ni #2554	11.5	0.57	13.2	0
Cr #2560	9.3	0.48	11.0	0
Cu #2321	11.5	0.20	13.0	0

2.6. *Electrical and Adhesion Properties*

The base metal conductors cannot be directly soldered or wire bonded. These serious short-comings can be overcome by utilizing intermediate metal layers. If ESL #9901, silver, pads are printed on top of dried prints of the Al, Cr or Ni and then cofired at 625°C, compatible films are formed. These composite overprinted films allow soldering as well as Al and Au wire bonding on the Ag surface. The developmental copper composition reacts with many of the silver and Pd/Ag top prints thus far tried, preventing adhesion and bonding studies from progressing further at this time. ESL gold, #8831A, can be overprinted or overlapped with the copper without noticeable interaction.

An electroless copper solution has been found to immersion coat the #2554, nickel, in 30 seconds. After rinsing the copper plated nickel, excellent solderability is obtained. Similar experiments with immersion tin plating of copper offer some promise of success. This work is still in progress.

Table III compares the adhesion and bonding properties of these conductors. In addition, water drop migration tests at 30 volts DC across a 2 mm gap are listed. #2554 Ni, #2590 Al, #2560 Cr, #2321 Cu, do not migrate under these conditions. The temperature coefficients of these base metals are highly positive. The nickel in particular has a TCR of close to 5000 ppm/°C. This suggests the possibility of using it for economical resistance thermometry. It would not be as stable as platinum is for that purpose. The relatively high resistivity of the chromium plus its high temperature stability suggests its possible use in heating element applications. In fact, several of the other metals offer similar possibilities for automotive applications.

For certain applications in severe environments, these conductors may be protected with glass coatings (overglazes) similar to #M-4030 dielectric.

2.7. *Heaters on Glass Substrates*

Ag coatings are used as the defroster heating elements on rear windows. A parallel line array of 100 square long conductive tracks between 2 bus bars was printed on soda-lime glass. ESL #590-C, Ag, and various base metals were compared using the pattern shown in Figure 4. The resistivity of the different conductors is shown in Table IV for firing temperatures of 625°C and 700°C.

Fine thermocouples were used to measure the glass surface temperatures between heater lines. Figures 5 and 6 are plots of applied voltage versus temperature reached in 10 minutes at each voltage. Because of its lower resistivity, a silver coated plate will reach a given

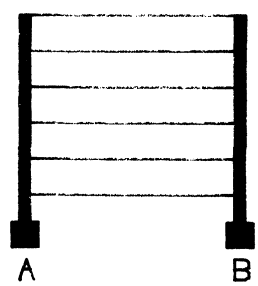


FIGURE 4 Defroster test pattern.

TABLE III
Typical properties of air fireable base metal conductors 625°C 45 minutes cycle—96% Al_2O_3 substrate

	#2254, Ni	#2590, Al	#2560, Cr	#2321, Cu
Resistivity (Ω/□)	0.055	0.040	0.900	0.024
Adhesion (5 mm × 5 mm) #9901 Ag overprint & cofired 90° peel test	2.5 Kg	1.2 Kg	5 Kg	—
Migration test[a] 2 mm gap, 30 volts	>20 min	>20 min	>20 min	>20 min
TCR (±200 ppm/°C) 25°C to 125°C	+4800	+3000	+1300	+3300
Wire bonding #9901 Ag overprint & confired				
1. Ultrasonic Al wire (1% Si) 25 micron diameter, grams	5–7	6–8	5–7	—
2. Thermosonic Au wire 25 micron diameter, grams	5–6	7–9	5–6	—

[a]Migration test is performed by applying a 30 VDC across a 2 mm gap pattern with a drop of deionized water in the gap. This test pattern is monitored with an ammeter. The time required to reach 1 milliamp is recorded.

TABLE IV
Resistance between A and B in defroster test pattern.

	Firing temperature, °C	
	625	700
#590-C Ag	0.073 Ω	0.045 Ω
#2554 Ni	1.060 Ω	0.477 Ω
#2590 Al	4.600 Ω	0.152 Ω
#2560 Cr	26.000 Ω	14.800 Ω
#2321 Cu	—	0.312 Ω

temperature, e.g., 50°C, at lower voltages. For the 625°C firing, 50°C is reached at 0.5 volt for Ag, 1.3 volts for Ni, and 2.4 volts for Al. After firing at 700°C, the Al drops sharply in resistivity and becomes much closer in characteristics to silver for use in such a defroster. Data are also presented on glass failure by cracking in Figure 6. It appears that heaters on glass using Al or Cu conductive tracks might be able to withstand hot spot temperatures of 250°C or more. The same glass plates using Ag heaters seem to be limited to about a 150°C maximum temperature. This problem is, of course, related to the wattage or power density and thermal gradients achieved in each case.

The base metal conductors offer promise as defroster elements on glass for automotive windows, refrigerator doors, and other uses on many different substrates. Some rearrangement of the heater geometry to compensate for the different resistivities and the low voltages available would be required. Ag overlayer soldering pads could be cofired at contact points corresponding to A and B in Figure 4.

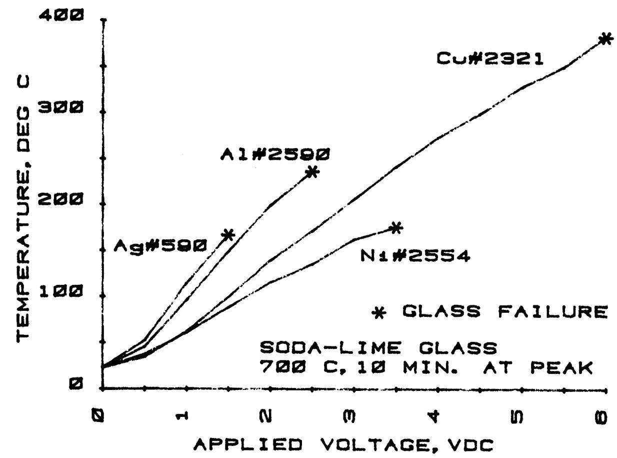


FIGURE 6 Temperature rise *vs.* applied voltage.

2.8. *Resistor Terminations*

The availability of a 625°C firing ruthenium-based resistor system, ESL #3100 Series allowed exploration of the possibility of using air-fireable base metals. Unfortunately, Al and Cu were quickly ruled out due to the formation of non-ohmic contacts. Ni has received the most study. Resistivities obtained with cofired Ni were close to those obtained with Pd/Ag terminations only for low resistivities. Figure 7 illustrates the negative geometry effects observed, which is more severe with the higher resistivities. This indicates that an appreciable contact resistance occurs with the nickel. This is also illustrated in Table V for 6 different resistivities.

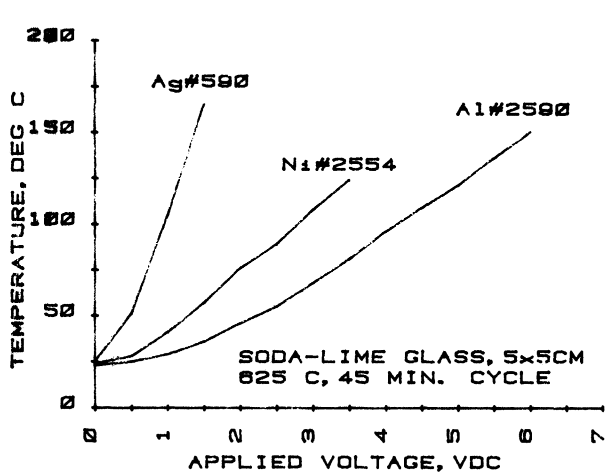


FIGURE 5 Temperature rise *vs.* applied voltage.

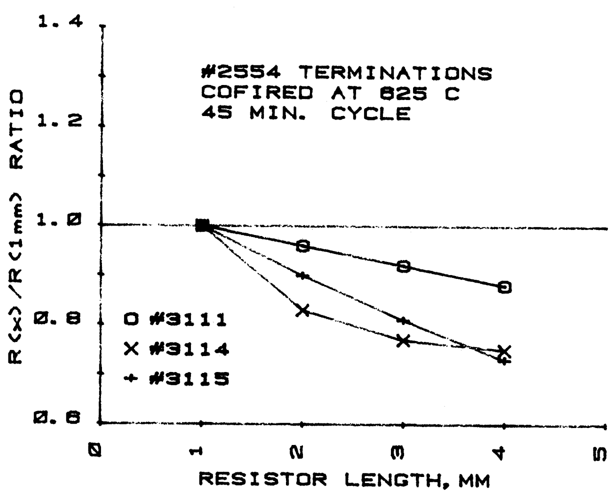


FIGURE 7 Geometry effect.

TABLE V
#3100 resistors with #2554 termination. Cofired at 625°C, 45 minute cycle (1.25 mm × 1.25 mm resistor size).

Resistor	Resistivity (Ω/□)	TCR (ppm/°C)
#3111	9.5	+300
#3112	255	+137
#3113	5,000	−92
#3114	38,100	−100
#3115	323,000	−184
#3116	11,500,000	−273

We have tried conductive terminations using Ni/Ag and Al/Ag compositions. Table VI presents the data for 1 K ohm and 100 K ohm/square pastes cofired at 625°C. If fairly high Ag concentrations are used, resistor properties of the 1 K ohm/square become comparable to the Pd/Ag control. For the 100 K ohm/square, some higher resistivities and more negative TCR's are still obtained.

With Ni or Al concentrations of 50 or greater weight percentages, non-ohmic chararacter develops rapidly and resistor properties show drastic shifts from standard. On the other hand, when 60% or more of Ag is present, reasonably good resistor characteristics are expected in the tests under way. Heat stabilities after baking at 150°C for several hundred hours are comparable to those obtained with Pd/Ag.

The combination of Ag with Ni or Cr does not lower their resistivities in a regular or predictable way. However, Al/Ag blends tend to be more predictable.

A preferred method of utilizing nickel (or several of the other metals) in resistor terminations is to use intermediate contacts of Pd/Ag. The overlapping Pd/Ag gives good ohmic contact to the resistors on one side and to the base metal on the other side. This is illustrated in Figure 8. This approach uses less precious metal than the use of mixtures as previously discussed. It has the disadvantage of requiring 2 conductor printings. However, the Pd/Ag and the base metals can be cofired in most cases. Using an overlapping pad of Ag or Pd/Ag is also feasible for forming solderable edge terminations (for lead attachment) and as wire bonding pads. We have also been able to print and fire gold pads on top of Ni and Al conductors. This permits eutectic IC die attachments.

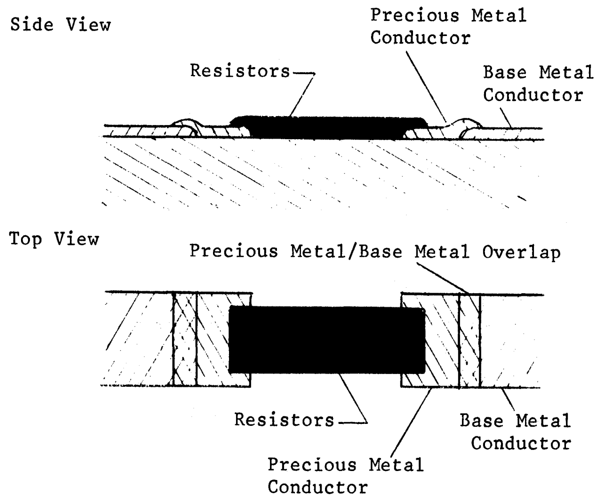


FIGURE 8 Resistor with overlapping terminations.

Extensive experiments are planned and some are in progress aimed at studying resistor performance using overlapping base metal-Pd/Ag contacts with both 625°C and 850°C resistor systems. This is expected to be a major effort, and will be reported upon at a later date.

2.9. *Terminations for Discrete Components and Parts*

One important area of utilization of base metals is for replacing part or all of the Ag used in terminations of titanate capacitors, thermistors, discrete resistors,

TABLE VI
#3100 resistors terminated with Ni/Ag and Al/Ag. Cofired at 625°C, 45 minute cycle.

	#3113		#3115	
	Resistance (Ω)	TCR (ppm/°C)	Resistance (Ω)	TCR (ppm/°C)
9635B (Control)	1.1K	+85	91.8K	−28
91025 Ni/Ag	12.8K	−100	956K	−276
91050 Ni/Ag	6.1K	−119	439K	−202
91075 Ni/Ag	1.3K	+80	161K	−100
93050 Al/Ag	1.4K	+92	256K	−159
93070 Al/Ag	1.3K	+81	216K	−118
93080 Al/Ag	1.1K	+92	194K	−128

TABLE VII
Disc capacitor[a] termination use. Fired at 625°C, 45 minute cycle.

	C (pf)	D.F. (%)
Control, (#9901 Ag)	26,600	2.1
#2554 (Ni)	25,730	5.1
#2590 (Al)	8,050	4.4
#2560 (Cr)	29,700	2.2
#2554 (Ni) (fired at 780°C)	26,200	7.8

[a]Barium titanate Z5U body, K = 10,000, courtesy of Sprague Electric Company.

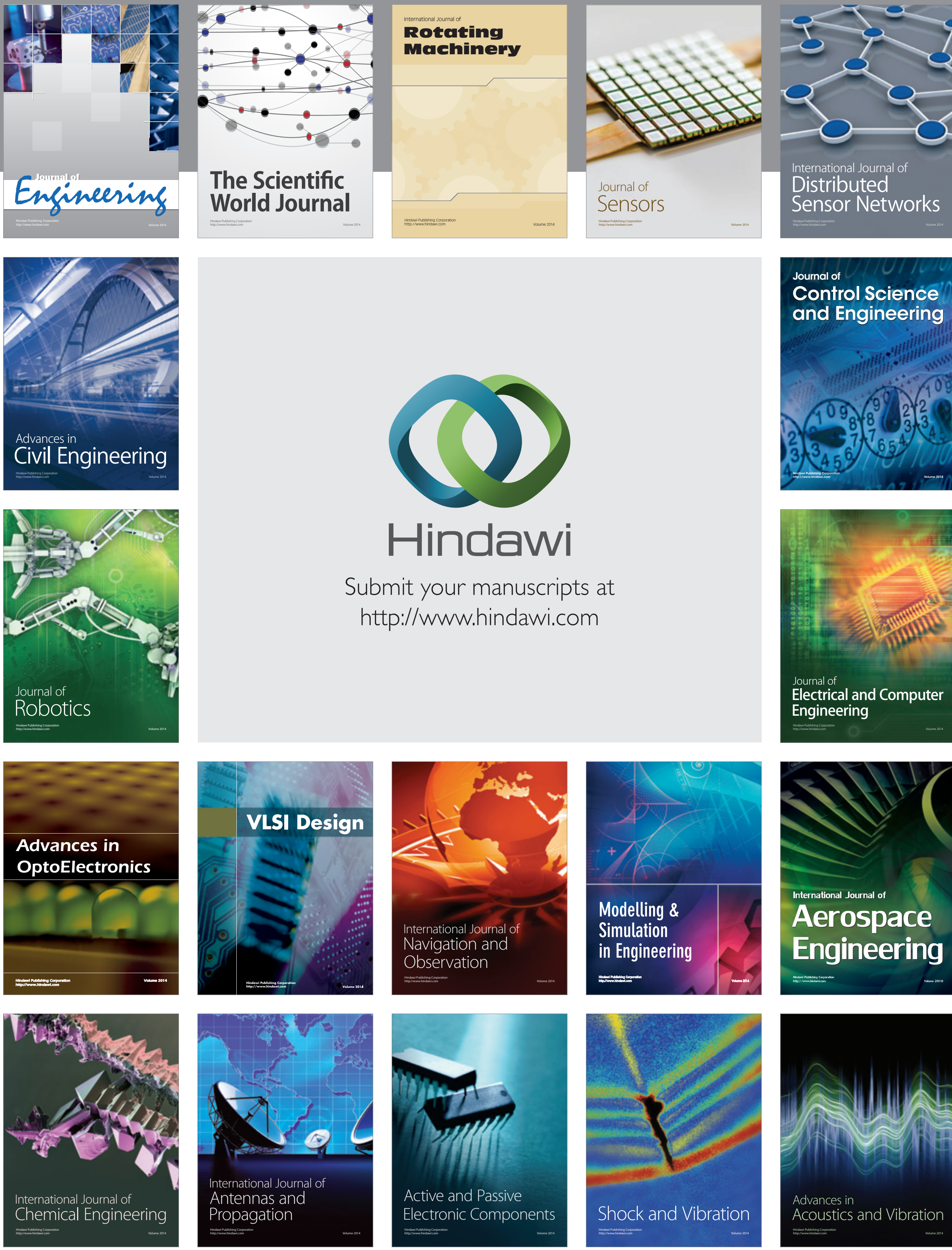
varistors, etc. In addition, metallization of glass and ceramic packages, seal rings, and other structural parts is of great interest. Many of these devices could be made with one or the other of the base metals, depending on the application.

Barium titanate capacitor bodies were terminated with Ni, Cr and Al on both sides of the discs. Firing was 625°C (45 minute cycle) and compared to a silver paste. Table VII lists the results obtained. The Cr and Ni gave capacitance values of the same order of magnitude as the Ag. The dissipation factor of the Cr terminated sample was better than that of the Ni sample. The ceramic used was a Sprague Z5U body with a K of 10,000. The Ni sample was also fired at 780°C. This caused the capacitance to remain the same, while the dissipation factor increased significantly. However, in experiments with a different titanate composition, there was a reversal in characteristics, and the Ni gave closer agreement than Cr did as compared to the Ag controls. It should be noted that the Al terminations caused very low capacitance values and did not show promise for this use.

Some work with zinc oxide varistors showed promising termination results with Al and Al/Ag compositions, The Cr and Ni, on the other hand, showed no merit with these varistors. A number of individually optimized frit formulations may be required to match the different varistor, thermistor and capacitor bodies in commercial use.

3. CONCLUSIONS

Several very promising base metal compositions offer opportunities for substantial cost savings in thick film applications. Some portion of the material cost savings is negated by the need to utilize an additional printing or electroless plating step. Available high speed printing and drying equipment permit such additional expenses to be minimized. Great care must be exercised in avoiding use-conditions that may affect reliability and stability. For these requirements, overglazes may be used. It must also be recognized that simple one-to-one substitution of Ag, Au, etc., is not *recommended.* Much more work is necessary before broad utilization of these air-fireable base metal conductors can be accomplished. However, the economic pressures of high prices and potential future shortages of some of the precious metals make it imperative to explore all alternatives.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