Aluminum-Clad Iron for Electron

"P-2 Iron," a European development, can be used in vacuum a substitute material for nickel and thus aid conservation of

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ASIDE from metals with extremely high melting point (tungsten, molybdenum and tantalum) nickel, without doubt, can be considered the most important metal in the electron tube industry.[1] For most applications nickel has a sufficiently high melting point, low vapor pressure, excellent fabricating characteristics, good corrosion resistance and still further, it may readily be degassed in vacuum by r-f or electron bombardment. The somewhat low coefficient of heat radiation of plain nickel sheets may be improved by carbonizing, thereby approaching the radiation coefficient of a black body. By virtue of these traits, nickel has become an indispensable raw material in the construction of radio receiving and transmitting tubes.

Search for Substitute

Since the European electron tube industries are dependent on the American or Canadian nickel supply, great efforts have been expended by these organizations to find a cheaper and more available substitute material. After many years of intensive research, shortly before World War II, the German metal industry developed a suitable material which became known as "P2-Iron." A first report on this development was published in 1948[2] simultaneously with the introduction of a similar material on the American market. The American counterpart consists of hot-rolled, low carbon rimming grade steel 0.080-in. thick which is cold-reduced to 0.040 in. The strip of this steel then is coated with an alloy of aluminum and 8% silicon in molten state and rolled to 0.125 mm (0.005 in.). Thereafter it is annealed in H_2 giving it a black finish and rendering it ductile and formable.

This American material, somewhat different from the European P2-Iron, is being used in several selected tube types by at least one manufacturer, and the production of this aluminized steel now is several tons per month.

Since aluminized steel has not as yet found the more wide-spread application that appears warranted, the following detailed story on the European development should help to clear up some of the issues still under consideration.

When considering substitute materials it is advisable to compare some of the other materials with respect to the properties of nickel. See Table I.

Aluminum, although readily available, has too low a melting point which prevents proper outgassing in vacuum. Its mechanical strength drops fast at elevated temperatures and further, its high chemical affinity to mercury vapor precludes its use in mercury vapor tubes or vacuum systems with mercury vapor diffusion pumps.

Oxygen-free *copper* (deoxidized or OFHC) [3,4] has acquired an important role in the construction of water-cooled transmitting power tubes, X-ray tubes and magnetrons. It is characterized by vacuum tightness, good adherence to glass and excellent heat conduction. However, for the construction of anodes of small and medium size radio tubes, copper is inferior to nickel as regards to vapor pressure, melting point, hot mechanical strength and coefficient of heat radiation. Also it is rather expensive and can be carbonized only with difficulties.

Disadvantage of Iron

Iron at a first glance appears as an inexpensive and readily available substitute for nickel. Its melting point is higher, its vapor pressure comparable to that of nickel and low carbon iron lends itself to deep drawing and spot welding. The coefficient of heat radiation is higher than that of nickel, but in a similar manner, iron surfaces like aluminum cannot be blackened by carbonizing. In spite of many favorable characteristics, iron is afflicted with an important disadvantage. Even after several days of degassing at high temperatures, iron continues to liberate at operating temperatures in the range of several hundred C° a small but ever-continuing amount of gas. It is obvious therefore, that iron cannot be used for small and medium size permanently-sealed vacuum tubes.

Since it was found that the gas content in iron diminishes with decreasing C-content, iron anodes and other electrode parts could be made by the powder metallurgy technique using sintered carbonyl iron powder.[6] However, the high manufacturing cost coupled with easy rusting of the cleaned and degassed parts rule out iron as a substitute for nickel, except for use in large tubes such as mercury-arc rectifier tanks.

For many years *graphite* has been used successfully for anodes of medium power-size transmitting tubes.[5] Graphite is endowed with a high melting point, low vapor pressure and excellent coefficient of radiation. However, its low mechanical strength requires heavier wall thickness. Its high gas content and high electric resistivity cause almost insurmountable difficulties in the construction and processing of small mass-produced radio receiving tubes.

P2-Iron was discovered by chance when carrying out tests aiming at the development of an iron without occluded gas. It was an occasional practice to insert aluminum into the liquid iron bath in the form of an aluminum-clad iron sheet.[9] Such bimetallic material has been used in Europe for packaging of canned goods, thereby reducing the amount of aluminum required. When inserting this bimetallic sheet it was observed that the color of the aluminum changed from a shiny to a very dark color. Upon closer examination it was found that this blackening is caused by a reaction between the iron base and the aluminum cladding, having a composition originally identified as $FeAl_3$. More recent X-ray diffraction investigations point to the probability of Fe_2Al_5. Depending upon the annealing conditions Debye diagrams reveal the

Tubes

tube manufacture as critical raw materials

presence of a still further composition tentatively identified as $Fe_2Al_4 = FeAl_2$.

At elevated temperatures there occurs an exothermic reaction which results in a coarse, opaque, dark-bluish surface of the aluminum covering. This dark surface is created not only by heating in air or by heating in a protective atmosphere, but also in vacuum. In fact, the cleanest surface can be produced by heating in the latter medium. When testing this aluminum-clad sheet as anode material in radio tubes an undesirable residue was found to deposit itself on the interior of the glass envelope. A further analysis showed this residue to be zinc. As a next step, a zinc-free aluminum was substituted and no further troubles were experienced. This new material consisting of an iron core with aluminum covering rolled on both sides, especially manufactured for vacuum purposes, was named P2-Iron. It was found to be usable without predegassing and being corrosion resistant, permitted storage without special provisions. The somewhat expensive carbonizing process[7] for nickel is very much simplified when using the P2-Iron, inasmuch as a blackening of the surface can be obtained merely by heating. In view of these characteristics the aluminum-clad iron material was used most extensively for anodes of radio receiving tubes in the European countries during the recent war.

Production of P2-Iron

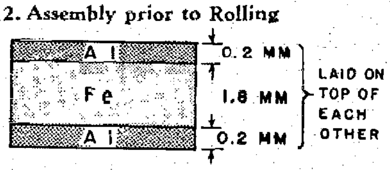
The production of P2-Iron for radio receiving tubes in sheet form of 0.15 mm thickness can be seen in Table II. The oxygen content and absence of silicon of the iron base is important. Also, the Si-content and absence of zinc in the aluminum is of greatest concern for the reasons explained above. The annealing temperature of the finished product must be held within the close limits shown on Table II. If standard iron is used for base material and non-alloyed aluminum for the covering, the blackening Fe-Al compound occurs at 430°C, which is lower than the

Table I: Properties of Nickel and Metals Used in Vacuum Technic

Properties		Ni	Al	Cu	Fe	P2-Metal
Specific Gravity	gm/cm^3	8.85	2.7	8.9	7.87	7.65
Melting Point	C	1452	658	1083	1528	1450(1)
Vapor Pressure at 800 C	mm Hg	$< 10^{-8}$	10^{-6}	10^{-4}	10^{-8}	10^{-6} (Al)
Tensile Strength annealed	Kg/mm^2	32-45	7-11	21-24	20-35(5)	→ 35(3) → 25(4)
Max. Temperature for const. load of 2 Kg/mm^2	C	600	80	270	450	420
Erichsen Ductility Test 0.5mm sheet	mm	11	9	13	8-10 11(6)	7(3) 3-4(4)
Coefficient of Radiation at 6650 A plain " carbonized	%	37.5 to 75	18-28 —	17 to 75	40-44 —	20-25 85
Spot welding	—	good with all metals incl. Mo.	bad	medium bad with Mo.	not as good as Ni	somewhat difficult
Corrosion Resistance without protection	—	very good	good in dry storage	good	very bad	same as Al
Degassing in Vacuum	—	good	very bad	bad espec. O_2	very bad with high C(2)	excellent
Degassing in H_2-Oven	—	good	very bad	possible if O_2 free	very bad with high C(2)	—

(1) Approx. Melting Point of Fe-Al compounds.
(2) Except with Al content.
(3) Prior to Annealing-Blackening } sheet thickness, 0.15mm.
(4) After Annealing-Blackening } sheet thickness, 0.15mm.
(5) Depending upon C-content.
(6) Carbonyl Iron

Table II: Manufacturing Procedure of P-2 Iron for Vacuum Use (0.15mm Total Thickness)

A. *Iron Base and Its Preparation*	
1. Iron Analysis % Balance Fe	C: 0.04-0.08 Mn: 0.1-0.6 S: 0.037 P: 0.039 Cu: 0.06 Si: none* O: 0.007 (in solid solution not as Oxide)
2. Ribbon Dimension (mm)	150 x 3.5
3. Pickling	H_2SO_4 10% concentr.
4. Rinsing & Cleaning	Washing, dry wire brushing
5. Cold Rolling	down to 1.8mm
6. Annealing	in closed pots
7. Surface Cleaning	wire brushing
B. *Preparation of Aluminum*	
8. Analysis of most important constituents %	Si: 1.0-1.5 Fe: 0.3-0.6 Zn: none
9. Dimensions (mm)	150 x 0.6
10. Rolling	without intermediate annealing to 0.2mm thick
11. Surface Treatment	brushing with steel wire brush on side contacting Fe
C. *Cold Rolling Process*	
12. Assembly prior to Rolling	
13. Cold Rolling without preheating of sheets	one pass, down to 0.9mm
14. Rolling Temperature due to cold working	180-200° C
15. Further rolling in convenient passes	Without intermediate annealing to 0.15mm : 5 vol. % Al per side, Al layer thickness about 7.5 μ (limits 5-20 μ)
16. Annealing in Electric Furnace	535° C ± 5° C in air 4 to 6 hours

* Standard commercial sheets showed 0.01-0.03% Si.

final annealing temperature of above 500°C. Such a material could not be annealed after rolling without creation of the Fe-Al compound a reaction which is undesirable until after final forming, spot welding, and degreasing of the electrode parts. By using iron and aluminum with compositions indicated in Table II, the reaction temperature between Al and Fe is raised to 680°C. Practice has shown that annealing of the P2-Iron material is necessary prior to fabrication of electrode parts in order to avoid deformation of such components during the outgassing and processing of vacuum tubes. Attention must be paid also that during the "cold rolling" process a temperature of 600°C is not exceeded such as may occur by too great a reduction or too fast a feed. In general, it was found that an equilibrium temperature of 180° to 200°C is sufficient for rolling and cold welding of the iron core with the aluminum cladding.

The thickness limits for the aluminum cladding was found to be 5 to 20 μ. If the aluminum layer is too thin, the aluminum may tear during wire brushing (see below), while with too thick a layer the aluminum may flow off in molten particles during final r-f heating inside the vacuum tube under simultaneous creation of Fe-Al compound flakes.

Further Handling of P2-Iron

Prior to using the P2-Iron, it is to be observed that there is an aluminum oxide layer on the surface of the P2-Iron which was produced during the preceding annealing process in air or in a protective atmosphere. If this oxide layer is not removed, the Fe-Al compound surface to be created later will not be as dark as it could be. Consequently, the P2-Iron is cleaned by wire brushing; for anodes the surface radiating toward the exterior only, both sides for radiating fins. The material thereby obtains a silky appearance on the cleaned side. It is important of course, that the aluminum cladding is not broken through. There is still another reason why sheets to be used for anode material are not wire brushed on the inside surface which faces the cathode. Without protective aluminum layer, oxygen might escape from the iron base and injure the oxide cathodes. Such oxygen may come from minute spots laid bare during brushing.

The P2-Iron ribbon usually is wire brushed automatically, followed by conventional shearing, punching, forming, drawing, etc., always watching the brushed side to face the exterior. The P2-Iron is somewhat harder and more resilient than nickel. Spot welding creates no difficulties, but the adjustment of the welder relative to current, pressure and time is different from the settings used for nickel and plain iron.[8] The welding electrodes should be cleaned more often to remove deposits of Al and Al_2O_3. When spot welding P2-Iron parts to other objects in vacuum Al-sputtering must be carefully avoided. It may be mentioned that welded P2-Iron sheets may readily be joined by spot welding with other metals (Ni, Cu, etc.) in fact, by using smaller currents than P2 sheets without blackened surface.

There is some difference of opinions as to the best method of blackening the finished formed and welded parts made of P2-Iron. The original method consists of degreasing the finished parts in trichlorethylene and then mounting them without pre-degassing inside the vacuum tube. Blackening is carried out by r-f during the final exhaust period by raising the anode temperature above 690°C which is slightly above the melting point of the aluminum (658°C). In spite of this temperature the aluminum will not flow off the iron core provided the aluminum layer is within the prescribed thickness limits and the r-f heating is not done too fast. Using the conventional bombarders, the r-f field penetration is considerably greater than the thickness of the aluminum cladding which results that the iron core is heated quickly and uniformly. Parts that are to have a good black surface should be kept below a temperature of 900°C because at this temperature, the degree of blackening diminishes whereby the coefficient of radiation drops from 85 to 60%. Manufacturers using above described method feel that during the blackening process more gas is absorbed than liberated, and as a result thereof the vacuum of the tube improves. The getter action is attributed to an increase in surface when creating the Fe-Al compound.

Table III: Most Important Bi-Metallic Iron Combinations Developed During 1938-45

NAME	ARRANGEMENT
P2	15 µ Al 120 µ Fe 15 µ Al
PN	15 µ Al 120 µ Fe 15 µ Ni
P1a	15 µ Al 15 µ Fe 120 µ EA-Fe
P1b	15 µ Al 120 µ Fe 15 µ EA-Fe

AL COMPOSITION PER TABLE II
Fe COMPOSITION PER TABLE II
EA-Fe IRON WITH 0.05 % C IN FORM OF SPHERISODIZED CEMENTITE, SEE FOOT NOTE 1

P-2 Parts Blackened

Others blacken the P2-parts prior to mounting them inside the vacuum tube by applying heat in vacuum or H_2. It is obvious, of course, that the temperatures are held between 680° and 900°C for the reasons stated above. This procedure may be necessary for small assemblies which when mounted inside of the vacuum tube cannot be reached by r-f, and also in the case where the Fe and Al alloy does not correspond with specifications given in Table II, causing the blackening temperature to be below the annealing temperature.

The blackened surface, if performed in H_2 has not as uniform an appearance as if carried out in vacuum. Moreover, using H_2 the aluminum is unnecessarily charged with H_2 which is difficult to remove.

The detrimental gas content of an anode made of P2-Iron is only a fraction of that of an anode made of carbonized nickel and same dimensions. Consequently there is a saving in processing time and temperature. The carbonizing process is much simpler than with Ni-anodes. It was for these reasons that P2-Iron became very popular for the production of small mass-produced radio receiving tubes. Experience showed that P2-Iron cannot be used in tubes with distillation cathodes. It appears that under the influence of H_2 a reaction occurs between the Ba-vapor and Al. Further, it was found that P2-Iron should not be employed in tubes with very small distances between anode

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and cathode because aluminum may distill over to the oxide cathode surface. For the latter application, a so-called "PN-Iron" was used, which is described below.

The PN-Iron has been used mainly for radiation-cooled anodes in small oxide cathode tubes. It consists of an iron core with aluminum covering on the side facing the outside and nickel cladding on the side facing the cathode, (Table III).

PN-Iron is manufactured as follows: Iron ribbon 20 mm thick, 250 mm wide and one (1) meter long of the same composition as specified for P2-Iron (Table II) and Mn-free nickel ribbon are laid on top of each other (well cleaned surfaces). This assembly is encased in a thin iron foil to prevent oxidation followed by heating to 1000°C in an electric oven. Then the assembly is hot rolled to 2.5 mm thickness using 7 to 9 passes. As a next step, the iron foil is removed by pickling. Thereafter aluminum is rolled on the remaining iron surface in the manner described in Table II. During the war, the Middle-European production of PN-material amounted to about 3 to 5 tons per month compared with 10 to 20 tons per month for P2-sheet.

For the sake of completeness, it may be mentioned that the Ni-shortage in Europe shortly after World War II caused a replacement of the Ni-cladding in PN-Iron by still other metals. The new material was named Pl-Iron and appeared in two forms, see Table III.

It may be interesting to note that the blackening effect of Fe and Al may be also produced by vacuum evaporation of Al on Iron. Other metal combinations give a similar effect; e.g.: Ni and Al, Mo and Al, etc., notwithstanding the fact that the combination of Fe and Al is very favorable, not only technically, but also economically.

It has been estimated that the Middle-European Electron Tube industry, during the years 1936 to 1944, saved about 500 tons of nickel by the use of P2-Iron. This quantity corresponds to about 250 million radio receiving tubes. In many cases it was possible to manufacture the vacuum tube at a considerable saving because of cheaper raw material costs, less expensive "Carbonizing" process, and shorter degassing and processing time. In other tubes a size reduction was possible due to the 85% radiation coefficient (black body 100%) compared with an optimum radiation coefficient of 75% for well-carbonized nickel.

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9. Aluminum was used as reducing agent for iron (original C-content in iron less than 0.09%). The end product showed about 0.05% Al. This iron material substantially gas free was sold under the name of "E-Iron" and "EA-Iron" respectively, when specially selected for anodes (C-content 0.05% in form of spheriodized cementite). This iron became obsolete with the advent of P2-Iron.

New Westinghouse Plants

The new electronic-tube division of the Westinghouse Co. is planning three new plants. Entering primarily into defense manufacturing, they will later produce transmitting, receiving, TV picture, and X-ray tubes. Sites are now being studied. The new division will be headed by E. W. Ritter with headquarters at Bloomfield, N. J.