

8 Cobalt in Electronics

Electronic technology can be divided into 8 sectors: Integrated circuits (packages of components on a micro-chip); discrete semi-conductors; vacuum tubes; magnetic tapes, resistors; transformers; capacitors.

Cobalt has a place in some of these and also in newer recording techniques such as thin film technology.

1. Integrated Circuits

An integrated circuit (IC) is a device which consists of a number of circuit elements formed in the surface of a chip of semi-conductor material (usually silicon). Modern ICs contain millions of circuit elements on a chip a few millimetres square.

Cobalt is used in a few ways in conjunction with ICs.

a) Contacts

Interconnections on chips are usually made with aluminium. However, smaller and smaller circuits have brought metal silicides into use because of their low resistivity, high thermal stability and good bonding properties. Pt/Si is generally used but CoSi_2 has been patented for this use.

b) Metal Leads

Gold is the common metal for marking mechanical electrical contacts. The gold used however is co-deposited with (15%) cobalt and this promotes far superior wear properties. This may not sound important in circuitry but cycling occurs and in fact failure can be caused by friction.

c) Packages

Whilst not strictly ICs, these are components packed onto a circuit board (PCB). The board can be plastic, beryllia, alumina or metal – copper, copper/tungsten, copper/Invar/copper, molybdenum, etc. – and cobalt is back in the picture. In the cobalt alloys section, the low and controlled expansion alloys were outlined – Superinvar which is 6% Co, 31% Ni, 63% Fe.

The thermal coefficient of expansion (TCE) of these alloys can be matched to a substrate and used to box in components by gluing ring frames over the circuits or brazing and finally sealing the whole unit to protect it.

2. Semi-Conductors

Cobalt has been used in the manufacture of semi-conductors devices containing gold or platinum. Cobalt can be diffused through the substrate and then gold or platinum is diffused in at a temperature sufficient to replace the cobalt but somewhat lower than would otherwise be required.

3. Magnetic Recording

Until a few years ago, magnetic recording was the main use of cobalt in electronics.

Magnetic recording materials use the magnetic properties of solids to store and retrieve information. Cobalt modified iron oxide (Fe_2O_3) particles are now the predominant material used in video tapes. Cobalt-containing magnetic recording media can be divided into two categories: i) oxides and metal particles or ii) metal films. It is perhaps worthwhile outlining the principles of recording (Figure 1).

A magnetic head (transducer) and the recording medium move in relation to one another. During recording, a varying current applied to the transducer coil, induces a magnetic field which magnetises a small region of the ferromagnetic recording medium. On play back, the varying magnetic fields on the tape pass the coil of

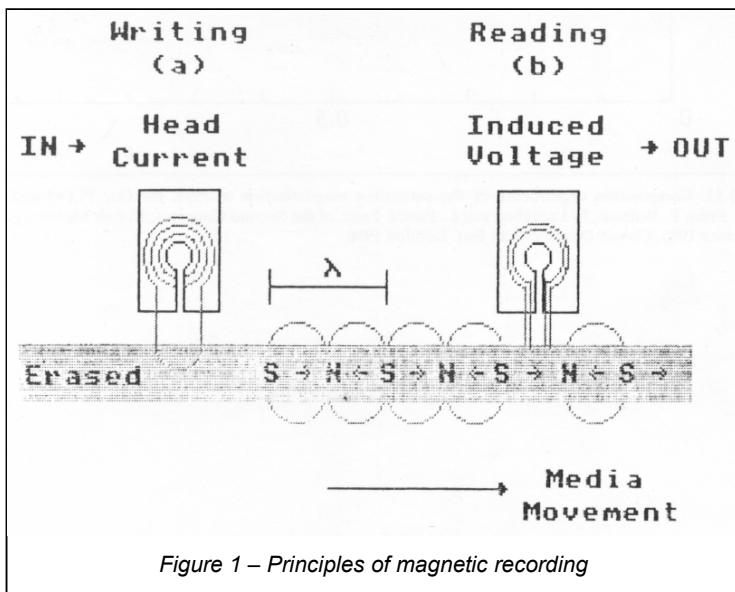


Figure 1 – Principles of magnetic recording

the transducer and reverse the process by inducing varying voltages in the coil. Quality in this area is of course measured by how close the output is to the original input (i.e. high fidelity).

The recording head needs to be a soft magnetic material which is easily magnetised to a high saturation level and then easily reversed, i.e. low coercivity. The recording media obviously needs to be a permanent magnet and to possess not too low a coercivity (otherwise strong fields would destroy the recording) but not too high or the recorder could never erase and reuse it.

Tapes typically have coercivities of 250-600 and up to 1,200 Oersteds (similar to Alnico magnets). Ideally,

each particle will be one magnetic domain (see magnet section). In practice, recording media consist of fine single domain particles immersed in a plastic binder or of continuously deposited films. In both cases, a strong substrate (terylene) provides mechanical strength.

Newer recording technologies developed over past few years mean that cobalt demand in these applications has fallen markedly. Future demand will be dependent on existing tape recording devices such as security monitoring. Hence cobalt demand will remain fairly constant at the level to sustain these applications.

4. Thin Films

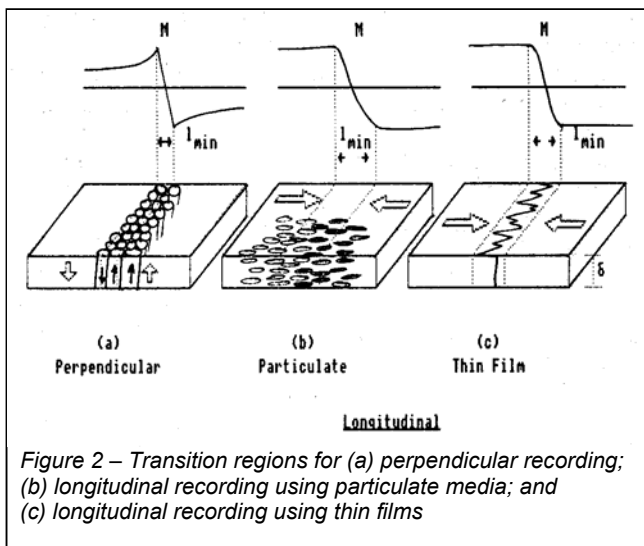


Figure 2 – Transition regions for (a) perpendicular recording; (b) longitudinal recording using particulate media; and (c) longitudinal recording using thin films

Newer processes have also employed cobalt. Thin metallic films with high coercivities have been deposited by various means – electroless plating, evaporating, sputtering, etc.

The films can be Co-P, Co-Ni, etc., but mainly **Co-Ni** for video recording. The alloy of 20 at %Ni is deposited at an oblique angle to the tape by evaporation and the properties vary with the angle of deposition. Floppy discs can also be made this way, although this is more difficult. Coercivities vary with the Co/Ni ratio from 400 to 1,000 Oe at high cobalt levels.

Cobalt/chromium alloys have more recently been used in what is termed perpendicular recording. This is a complex subject but is illustrated by Figure 2.

The Co/Cr alloys used are sputtered onto a film and produce columnar structures. The

Co/Cr alloys are mutually soluble and a range of values of coercivity from 100-2,000 Oe can be obtained making them a very versatile medium.

Future

Magnetic recording and other electronic applications are a growth area for cobalt. Although quantities may not be large in each film, the amount of recording material now being produced will ensure cobalt's future.

Further Reading

Cobalt in Electronic Technology – CDI, 1988.

8.1 Cobalt in Batteries

Batteries are electrochemical devices that convert chemical energy into electrical energy. Their major components include an anode and a cathode which are separated by a non-conductive separator that will allow the flow of ions but not the flow of electrons, a case and an electrolyte (Figure 1). In battery terminology, the cathode is the electrode through which the electrons enter a cell and the anode is the electrode through which they leave the cell. When the battery is discharged, electrons move from the anode to the cathode as ions move from the cathode to the anode.

Batteries can be divided into two types – primary and secondary. In primary batteries, the chemical energy of its constituents is changed when the current is allowed to flow and this type cannot be recharged because the chemical reactions are irreversible.

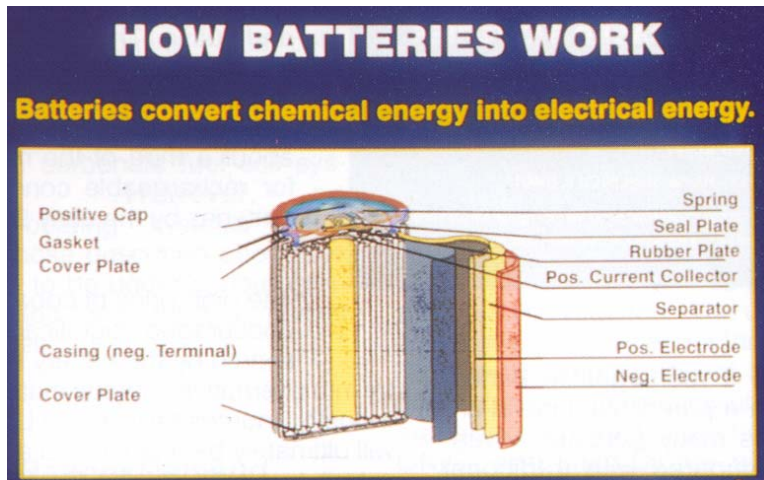


Figure 1

In secondary batteries, the application of an electrical current brings about chemical changes which are reversed as the cell discharges. Such batteries can be recharged hundreds of times before degradation occurs.

For many years battery technology advanced very slowly compared to other areas. However, since the mid 1980's, the reduced size and portable nature of electronic devices such as camcorders, portable telephones and laptop computers has generated enormous demand for high capacity, rechargeable batteries to power these devices. For instance, in the

developing countries, there has been little interest in establishing a hard-wired communication infrastructure and portable telephones are being used to meet communications needs.

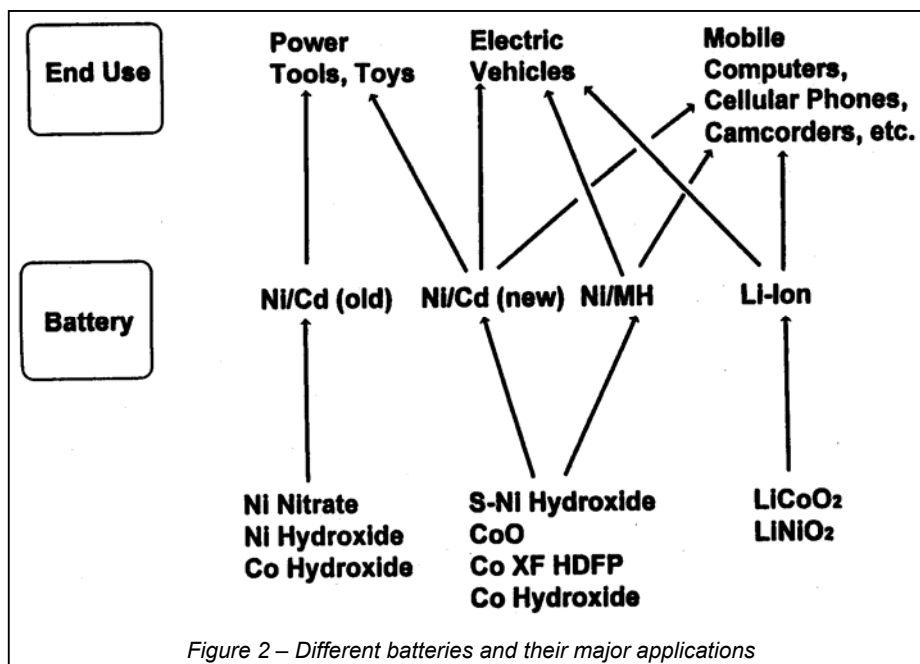
This trend has been particularly advantageous to cobalt in that the three high energy density batteries best suited to portable devices use substantial amounts of cobalt.

In the last few years, demand for portable rechargeable electronic devices has grown rapidly, such that the use of cobalt in these applications has more than doubled. Basically, there are three technologies which are in order of increasing cobalt content and growth opportunity:

- Nickel-Cadmium (Ni-Cd)

- Nickel-Metal Hydride (Ni-MH)
- Lithium ion (Li-ion)

Figure 2 summarises the major applications where these batteries are used and the various materials used in each.



Nickel-Cadmium Batteries

In the late 1980s and early 1990s, Ni-Cd batteries were the most common rechargeable batteries used in portable electronic devices as a result of their low cost, ready availability and established technology. In Ni-Cd cells, cobalt is used only in the positive electrode (cathode) where it enhances performance.

The amount of cobalt used is usually about 1% by weight of the nickel hydroxide but can be up to 5% in high performance batteries. The cathode is either a nickel foam filled with spherical nickel hydroxide or a sintered nickel substrate impregnated with nickel hydroxide. Cobalt, in the form of fine powder, oxide or hydroxide, is used as additive in these electrodes for the following reasons:

- It drastically improves the conductivity of the nickel electrode
- It mechanically stabilises the electrode by inhibiting the formation of γ -NiOOH and reduces the rigidity of the nickel hydroxide deposit
- It increases the potential for electrolyte decomposition

The ability to deliver high currents makes them particularly suitable for portable power tools. However, there are a number of problems associated with these batteries which means that little future growth is anticipated. The major problems are:

- The so-called memory effect whereby loss of battery capacity occurs as a result of recharging the battery before it is fully discharged
- Over-discharging which causes cells to develop internal short circuits and cause the battery to run down prematurely and eventually take no charge at all

The specific energy output is about 50% less than the nickel-metal hydride and lithium ion cells.

Nickel-Metal Hydride Batteries

The advent of Ni-MH rechargeable batteries can be attributed to Phillips Electronics in 1969 who were carrying out research to develop improved powerful magnets based on SmCo_5 . Related studies showed that the compound LaNi_5 could store large amounts of hydrogen in a highly reversible manner at room temperature. The significance of this discovery led to their use as rechargeable battery negative electrodes. Since 1988, metal hydride (MH) the so-called "hydrogen storage alloys" have been commercialised in several applications. Early alloys used were of the CaCu_5 type, most notable LaNi_5 . Such alloys suffered from poor cycle life, internal cell pressure and corrosion as a result of the simple single-phase natures of these hydride alloys. The development of multi-component multiphase alloys overcame the problems. It was also found that the addition of cobalt to these rare-earth/Ni alloys substantially enhanced the cells' cycle life. The addition of cobalt also tends to increase hydride thermodynamic stability and inhibits corrosion. Today's alloys from the LaNi_5 family are generally complex materials containing six to eight elements with complex phase structures.

Cobalt-containing alloys are of the type V-Ti-Zr-Ni and contain up to 15% cobalt. However, alloy development continues and new magnesium based hydrogen storage alloys are currently under development for a generation of cheaper lighter nickel-metal hydride cells.

The first Ni-MH batteries used the same nickel electrode as that of the positive electrode in Ni-Cd cells.

The addition of fine cobalt powder or cobalt oxide to the pasted nickel hydroxide electrode serves to provide some reserve capacity in these electrodes (to prevent gas evolution). The fine cobalt is oxidised to CoOOH during charge and remains in the cobalt(III) form during discharge thus providing reserve capacity to the MH electrode.

The combination of a rechargeable nickel electrode and a metal hydride electrode results in a battery system that is superior to Ni-Cd. It has greater specific energy – i.e. a lighter battery, greater volumetric energy density – i.e. a smaller battery with less environmental impact because of the absence of cadmium and it does not exhibit the memory effect which can reduce the life of Ni-Cd batteries.

Ni-MH batteries operate at 1.2 volts, the same as Ni-Cd types, but possess a much higher capacity. They are used extensively in portable computers, mobile phones and camcorders and have largely displaced Ni-Cd batteries in these applications.

Lithium-Ion Batteries

Rechargeable batteries based on a metallic lithium anode have many theoretical advantages over other systems but early designs failed commercially as a result of the reactivity of lithium metal which resulted in a number of battery fires. The problem has been overcome by replacing the lithium anode with a non-metal such LiC_6 which is capable of storing and reversibly exchanging a large quantity of lithium ions. In this way, rather than lithium plating and stripping as in conventional lithium batteries, the electro-chemical process at the anode is the uptake of lithium ions during charge and their release during discharge. If the cathode is also non-metallic such as LiCoO_2 , capable of reversibly exchanging lithium ions, the entire battery process involves the shifting of lithium ions back and forth between electrodes. The lithium-ion rechargeable battery is also called the swing cell because of this action.

The Li-ion battery is the most advanced of the three systems. Unlike the 1.2V Ni electrode systems, Li-ion cells operate at about 3.7V and rely on lithium ions moving through organic solvents rather than protons in water to balance external charge transfer. A single lithium-ion cell replaces three Ni-Cd or Ni-MH cells in most applications. The much higher voltage and very light negative electrode (LiC_6) explain why this is the most advanced rechargeable system and the one preferred for high power applications such as portable computers which often use more cells per device.

Of the three systems, the Li-ion battery contains by far the greatest amount of cobalt per cell. The cathode active material contains 60% cobalt rather than the 5-15% of Ni electrode cells and accounts for about 50% of the weight of the cathode.

LiCoO₂ is the preferred materials but both LiNiO₂ and LiMn₂O₄ can also be used. Recent research by the major battery manufacturers has resulted in LiNiO₂ and LiMn₂O₄ based rechargeable batteries with comparable properties to LiCoO₂ based batteries being produced. Cost has been cited as the major driver for substitution.

In early 1998, when cobalt prices were high, some manufacturers indicated manganese-based systems would sell for 20-40% less than cobalt-based. At this particular time, partial substitution for cobalt by nickel and/or aluminium was also being investigated. Now that cobalt prices are lower, these factors need re-assessing. However, scientists working on the development of 50-100 Ah batteries for the USAF and Canada's Department of National Defense preferred LiCoO₂ systems to LiNiO₂ and LiMn₂O₄ for a number of technical reasons.

Market

The use of cobalt in rechargeable batteries grew enormously between 1995 and 2000. Estimates suggest growth went from about 700 tonnes/annum to nearly 5,000 tonnes/annum during the period. The severe worldwide economic recession beginning towards the end of 2001 resulted in a massive drop in demand in the telecommunications industry. The fall in demand for portable telephones resulted in up to a 20% fall in the demand for cobalt in these applications.

However, growth in demand for mobile phones has increased enormously since 2002 and in 2005, it is estimated that battery applications accounted for nearly 25% of worldwide cobalt demand, about 12,000 tonnes.

Substitution for LiCoO₂ by manganese and nickel based systems will undoubtedly soar in the next few years but the rate of substitution will be largely dependent on the price of cobalt. However, the projected increased in demand for mobile phones will ensure a steady increase in demand for cobalt in rechargeable batteries in the next few years.

The increase in popularity for hybrid vehicles is expected to substantially increase demand for cobalt in rechargeable batteries in the next five years.