Steel making down the ages

Chromium steel – like the tool steel we know today – was made in Persia a millennium ago


Chromium steel from the site in Iran

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Just as the Bronze Age and Iron Age marked stages of development since ancient times, widespread use of steel is the mark of the modern age. And yet, the material has been known for a long time.

What has been known for long, however, is iron in a crude form. Its refinement into steel, with the addition of different substances to improve its properties, is a modern development. Yet, Rahil Alipour, Thilo Rehren and Marcos Martinón-Torres, from University College, London, The Cyprus Institute, Nicosia and the University of Cambridge, UK, write in the *Journal of Archeological Science*, that over 10 centuries ago, the Persians could make chromium steel, a sophisticated material we have believed to be of recent origin.

In the ancient world, the discovery of fire led to baking pottery and extracting metal from ores. As the fires were wood fires, only metals that have low melting points could be extracted. Typically, these are copper and tin, and the alloy, which is bronze. There was also silver and gold, but these were rare and not sturdy or useful. It was only after the discovery of coal, and higher temperatures became possible, that iron could be extracted. The discovery of iron expanded the scope of agriculture, hunting, attack and defence, and the Iron Age (1200 to 600 BCE) is another phase of civilisation.

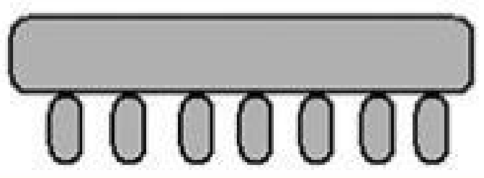
Iron occurs in the ore in combination with oxygen, in the form of its oxides. The process of extracting the metal is to heat the ore with carbon, so that the oxygen atoms change partners and become carbon dioxide, leaving behind the metallic iron. As we can expect, there is much carbon left in the material created -- in fact, there is 3.8-4.7 per cent of carbon, and the carbon is dissolved in the iron. This crude form of iron, just extracted from the ore, is called *pig iron* and is the starting point for a purer form of iron, which is called *wrought iron*.

Thanks to the high carbon content, *pig iron* is brittle and of limited utility. It is purified by melting and exposure to a strong current of air, while it is stirred and agitated, when impurities are oxidised and can be removed. Ironically, pure iron is ductile, or easily bends and changes shape. The solution is to add carbon, but less than what there is in pig iron, to give it strength.

The crystalline structure of iron is "cubic", either with atoms at the corners of cubes or in the middle of the faces of the cubes. The result is that the cubes slide over one another. Adding other substances, mainly carbon, helps hold the cubes together and improves the strength of iron. Iron with up to 2.4 per cent of carbon is steel, the wonder material of the modern world. Not that steel was not made earlier, but working with iron, in coal furnaces, was tiresome, and steel was made only for special purposes, like swords or suits of armour. This changed with coking coal and plentiful coal, when mining methods improved. Better grades of furnaces led to more production of steel, and there was expansion in many fields, of construction and manufacture, when steel was freely available.

Pig iron

The first, crude melt, when iron is made, used to be poured into sand moulds that were shaped like a stem with branches – it looked like a sow suckling piglets. The branches, which were broken off for purification or working on, were called "pigs".



There was, nevertheless, the industry of steel making in the ancient world. The method used was to mix *pig iron* and *wrought iron* in the melt, to reduce the carbon content by dilution. As the process was in a crucible, the product is called *crucible steel*. The paper in the Journal of Archeological Science says there is evidence for two *crucible steel* making traditions – the wootz steel made in south India and Sri Lanka, since the third century BCE, and in later centuries, in Central Asia (the Persian *pulad*).

Wootz steel from India became famous for its strength and hardness and was in demand in the West for the manufacture of Damascus steel and swords for the Crusades. The Indian method used ores from particular sources, with a number of ingredients with the ore during smelting, followed by reducing the carbon content by dilution with purer materials. The reason for the strength, and very high corrosion resistance (the Iron Pillar near Delhi, of the fourth and fifth century AD, for example) is understood to be partly the organic materials added during smelting, but largely the trace impurities present in skeins of ore that were used. When those sources depleted, the supply of this steel also came to a stop.

As for the industry in Central Asia, the paper discusses archeological finds in a site, Chahak, in southern Iran, which is described in historical reports as a centre of steel production. A specific report is the work, *al-Jamahir fi Marifah al-Jawahir* (*A Compendium to Know the Gems*), by Abu Rayhan al-Biruni, the famous scientist, scholar, historian, theologian, traveller and linguist, around the turn of the first millennium. While other reports speak of steel being made in Chahak, Al Biruni describes the process used and the materials, some of which are not identified, as additives.

The paper says that most crucible steels found at historical sites have greater carbon content than ideal, some phosphorus, which adds some properties, but scant traces of other metals like manganese, vanadium or chromium, which we find in modern steels. In the samples of steel, as in suits of armour, swords, blades and daggers, where we do find traces of such materials, we cannot be sure of their place or time of origin, the paper says. And the sole plausible instance of an object with chromium content greater than one per cent has not been matched with evidence that the chromium was added during steel production.(It is in this context that the authors of the paper report physical evidence of production of low chromium *crucible steel*, with conscious addition of a chromium mineral, in Chahak, the only known archeological site in present day Iran. While the site has been mentioned in manuscripts, no excavation was conducted until the present work. The current study has discovered and analysed *crucible steel* making waste, rubble of broken crucibles, with the slag that is left after smelting, and evidence of smithing workshop and furnaces.

How did it disappear?

We can understand that the quality of wootz steel was not the result of process design and hence died out. But this is not true of chromium steel of ancient Persia, where there was deliberate addition of a chromium mineral. A reason its use declined could be the dark years and breaking of communications that followed the sacking of Constantinople, the rise of the Ottomans and the Black Death, in the 12th and 13th centuries.

Analysis of bits of steel that were found indicated positive chromium content at levels that affect the performance of steel. Again, there was high content of chromium oxide in the slag, which separates from the metal during smelting. However, there was no chromite in the material of the crucibles or in the smithing workshop. The presence of chromium in the products must hence arise from deliberate addition, the paper says.

Modern stainless steel is an alloy of steel with chromium as an important component. The chromium adds to strength, raises heat resistance and creates a surface film that prevents the formation of iron oxide, and hence corrosion. Modern steel is the result of metallurgy and scientific advances of recent times. It seems some method of product development in Persia had reached the same place a thousand years ago.

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TOMORROW'S BODY ART

According to exciting new research, dynamic tattoos could soon become reality and warn wearers of health threats

CARSON J BRUNS

In the sci-fi novel *The Diamond Age* by Neal Stephenson, body art has evolved into "constantly shifting mediatronic tattoos" – in-skin displays powered by nanotech robopigments. In the 25 years since the novel was published, nanotechnology has had time to catch up, and the sci-fi vision of dynamic tattoos is starting to become a reality.

The first examples of colour-changing nanotech tattoos have been developed over the last few years, and they're not just for body art. They have a biomedical purpose. Imagine a tattoo that alerts you to a health problem signalled by a change in your biochemistry, or to radiation exposure that could be dangerous to your health.

You can't walk into a doctor's office and get a dynamic tattoo yet, but they are on the way. Early proof-of-concept studies provide convincing evidence that tattoos can be engineered, not only to change colour, but to sense and convey biomedical information, including the onset of cancer.

Signalling biochemical changes

In 2017, researchers tattooed pigskin, which had been removed from the pig, with molecular biosensors that use colour to indicate sodium, glucose or pH levels in the skin's fluids.

In 2019, a team of researchers expanded on that study to include protein sensing and developed smartphone readouts for the tattoos. This year, they also showed that electrolyte levels could be detected with fluorescent tattoo sensors.

In 2018, a team of biologists developed a tattoo made of engineered skin cells that darken when they sense an imbalance of calcium caused by certain cancers. They demonstrated the cancer-detecting tattoo in living mice.

UV radiation sensors

My lab is looking at tech tattoos from a different angle. We are interested in sensing external harms, such as ultraviolet radiation. UV exposure in sunlight and tanning beds is the main risk factor for all types of skin cancer. Non-melanoma skin cancers are the most common malignancies in the US, Australia and Europe.

To help address this problem, we developed an invisible tattoo ink that turns blue only in UV light, alerting you when your skin needs protection. The tattoo ink contains a UV-activated dye inside of a plastic nanocapsule less than a micron in diameter – or thousandth of a millimetre – about the same size as an ordinary tattoo pigment.

The nanocapsule is needed to make the colour-changing tattoo particles large enough. If tattoo pigments are too small, the immune system rapidly clears them from the skin and the tattoo disappears. They are implanted using tattoo machines in the same way as regular tattoos, but they last for only several months before they start to degrade from UV exposure and other natural processes and fade, requiring a "booster" tattoo.

I served as the first human test subject for these tattoos. I created "solar freckles" on my forearm -- invisible spots that turned blue under UV exposure and reminded me when to wear sunscreen. My lab is also working on invisible UV-protective tattoos that would absorb UV light penetrating through the skin, like a long-lasting sunscreen just below the surface. We're also working on "thermometer" tattoos using temperature-sensitive inks. Ultimately, we believe tattoo inks could be used to prevent and diagnose disease.

Temporary high-tech tattoos

Temporary transfer tattoos are also undergoing a high-tech revolution. Wearable electronic tattoos that can sense electrophysiological signals like heart rate and brain activity or monitor hydration and glucose levels from sweat are under development. They can even be used for controlling mobile devices, for example shuffling a music playlist at the touch of a tattoo, or for luminescent body art that lights up the skin.

The advantage of these wearable tattoos is that they can use battery-powered electronics. The disadvantage is that they are much less permanent and comfortable than traditional tattoos. Likewise, electronic devices that go underneath the skin are being developed by scientists, designers and biohackers alike, but they require invasive surgical procedures for implantation.

Tattoos injected into the skin offer the best of both worlds: minimally invasive, yet permanent and comfortable. New needle-free tattooing methods that fire microscopic ink droplets into the skin are now in development. Once perfected they will make tattooing quicker and less painful.

Ready for everyday use?

The colour-changing tattoos in development are also going to open the door to a new kind of dynamic body art. Now that tattoo colours can be changed by an electromagnetic signal, you'll soon be able to "programme" your tattoo's design, or switch it on and off. You can proudly display your neck tattoo at the motorcycle rally and still have clear skin in the courtroom.

As researchers develop dynamic tattoos, they'll need to study the safety of the high-tech inks. As it is, little is known about the safety of the more than 100 different pigments used in normal tattoo inks. The US Food and Drug Administration has not exercised regulatory authority over tattoo pigments, citing other competing public health priorities and a lack of evidence of safety problems with the pigments. So US manufacturers can put whatever they want in tattoo inks and sell them without FDA approval.

So far, there is no evidence that tattoos cause cancer, and one study even found that black tattoos protect against UV-induced skin cancer. Still, many tattoo inks contain or degrade into substances that are known to be hazardous, and health complications including infection, allergy and granuloma have been found in about two per cent of tattoos. More research is needed to understand the long-term effects of nano and microimplants in the skin in general.

A wave of high-tech tattoos is slowly upwelling, and it will probably keep rising for the foreseeable future. When it arrives, you can decide to surf or watch from the beach. If you do climb on board, you'll be able to check your body temperature or UV exposure by simply glancing at one of your tattoos.

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PLUS POINTS

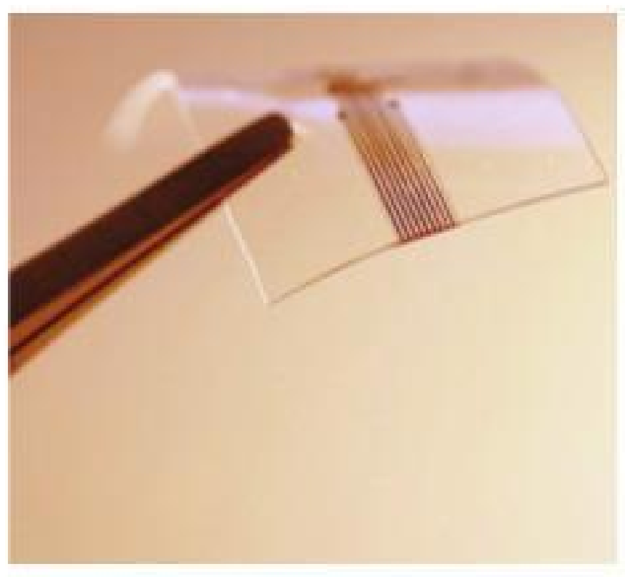
3D-printed neural implants

Linking the human brain to a computer is usually only seen in science fiction, but now an international team of engineers and neuroscientists at the University of Sheffield (UK), St Petersburg State University (Russia) and Technische Universität Dresden (Germany) have harnessed the power of 3D printing to bring the technology one step closer to reality.

In a new study published in *Nature Biomedical Engineering*, the team led by Professor Ivan Minev (department of automatic control and systems engineering, Sheffield University) and Professor Pavel Musienko (St Petersburg State University), have developed a prototype neural implant that could be used to develop treatments for problems in the nervous system.

The neural implant has been used to stimulate the spinal cord of animal models with spinal cord injuries and now could be used to develop new treatments for human patients with paralysis. The proof of concept technology has been shown in the study to also fit well on the surface of a brain, spinal cord, peripheral nerves and muscles, hence opening possibilities in other neurological conditions.

Linking the human brain to a computer via a neural interface is an ambition for many researchers throughout the worlds of science, technology and medicine, with recent stories in the media highlighting efforts to develop the technology. However, innovation in the field is hampered by the huge costs and long development time it takes to produce prototypes – which are needed for exploring new treatments.



The technology promises great potential to bring new medical treatments for injuries to the nervous system based on a fusion of biology and electronics. The vision relies on implants that can sense and supply tiny electrical impulses in the brain and nervous system.

The team has shown how 3D printing can be used to make prototype implants much quicker and in a more cost effective way in order to speed up research and development in the area. The implants can be easily adapted to target specific areas or problems within the nervous system.

Using the new technique, a neuroscientist can order a design which the engineering team can transform into a computer model which feeds instructions to the printer. The printer then applies a palette of biocompatible, mechanically soft materials to realise the design. The implant can be quickly amended if changes are required, giving neuroscientists a quicker and cheaper way to test their ideas for potential treatments.

Ivan Minev, professor of intelligent healthcare technologies at the University of Sheffield's department of automatic control and systems engineering, said, "The research we have started at TU Dresden and continuing here at Sheffield has demonstrated how 3D printing can be harnessed to produce prototype implants at a speed and cost that hasn't been done before, all whilst maintaining the standards needed to develop a useful device. The power of 3D printing means the prototype implants can be quickly changed and reproduced again as needed to help drive forward research and innovation in neural interfaces."

The researchers have shown that 3D printers can produce implants that can communicate with brains and nerves. Following this early work, the team aims to demonstrate how the devices are robust when implanted for long periods of time.

The team's ambition, however, is to go to the clinic and open up the possibilities of personalised medicine to neurosurgeons. Minev said, "Patients have different anatomies and the implant has to be adapted to this and their particular clinical need. Maybe in the future the implant will be printed directly in the operating theatre while the patient is being prepared for surgery."