

Subtle niobium

Michael Tarselli reflects on the intriguing characteristics of a rather underrated element, niobium, in its 'missing' and existing forms.

Pity poor niobium — it's suffered identity crises for the better part of the past two centuries. Originally dubbed columbium by discoverer Charles Hatchett in 1801, niobium was exceedingly difficult to separate from its group 5 neighbour tantalum, as they possess very similar chemical properties. Nearly 50 confused years passed before Heinrich Rose 'rediscovered' niobium in the mineral tantalite in 1844. He named it after the goddess Niobe, whose father, the mythical king Tantalus, is the namesake of its elemental cousin. The name columbium, however, was to linger alongside niobium until the 1950s. Several other elements believed to have been isolated from tantalite were later shown to be either niobium or mixtures of niobium and tantalum. In fact, Hatchett's columbium itself was also probably an Nb–Ta mixture.

Much of the niobium believed to exist on Earth — from compositional comparison with meteorites — is actually 'missing'; geologists theorize¹ that it may be contained in deep silicate reservoirs in the planet's core. Unequal distribution in the Earth's crust of the remainder — mostly in Brazil and Canada — has prompted a vigorous search for new deposits. Many have recently been found in geopolitically sensitive areas, such as southern Afghanistan² and the Democratic Republic of the Congo.

Despite this avid interest, niobium manages to fly under the very radars it helps to build. In practical applications — for example as a steel strengthener, a refining additive or a mineral acid for metalwork — it always plays second fiddle to some other transition metal. Yet element 41 endows many materials with noteworthy properties. Niobium–zirconium alloys³ have been incorporated in non-toxic, non-immunogenic dental amalgams and bone implants. Benzyl alcohol-modified niobium nanoparticles can initiate reversible



addition–fragmentation chain transfer (RAFT) polymerizations under irradiation with visible light, yielding well-controlled chains of the versatile poly(methyl methacrylate) polymer. Doped niobium oxides, called 'niobates', serve as thin-film capacitors for solar cells and promote biofuel refining on zinc supports. Alloyed with tin or strontium, niobium exhibits superconductor-like behaviour promising for energy storage materials. Your mobile phone may well contain niobium nitride, a superconductor used in some tiny piezoelectric devices.

With five electrons in its outer valence shell, niobium enjoys rich redox chemistry through oxidation states ranging from –1 to +5. This shell can be plucked away to reveal a highly oxophilic [Kr] core, useful as a halide transfer agent, oxidant, or even to activate C–H bonds. In a recent catalytic effort, a Nb(III) complex has been shown to activate fluoroarenes' C–F bonds⁴ — probably through two niobium complexes arranging in an 'inverted sandwich' around the benzene ring, twisting it with η^6 coordination into an almost cyclohexane-like geometry, thus removing its aromaticity and facilitating C–F cleavage.

Ask most organic chemists about niobium-promoted reactions and you'll get blank stares — its organic chemistry just hasn't been widely explored. But niobium still finds synthetic use in surprising places. For example, the niobium(V) to (III) reduction can promote reductive couplings⁵ of alkynes and various electrophiles — much like that of manganese, titanium, or nickel. In heterogeneous catalysis, niobium

nanoparticles and clays serve as solid supports for oxidative transformations. Homogeneous catalysis with niobium(V) chloride can deprotect methyl ethers, perform Friedel–Crafts cyclizations and snap together multicomponent reactions. A recent study⁶ capitalizes on niobium(V)'s highly oxidizing nature to decontaminate warfare agents: combined with hydrogen peroxide, niobium–saponite clays can readily convert mustard gas simulants into non-toxic products.

Niobium also inspires beautiful chemical artistry. Pamela Zurer wistfully describes⁷ how refractive, shimmering surfaces can be 'dialled in' on the surface of bare niobium metal using anodizing baths to generate thin coatings of niobium oxide. Different layer thicknesses produce different colours. This technology has served both art and commerce, with Austria minting green, pink, or purple collectable Euro coins (pictured).

What does the future hold for this underappreciated metal? No doubt its uses in energy storage and organic synthesis will increase, but perhaps most exciting is its role in building novel inorganic frameworks — zeolites, semicrystals and core–shell particles — for biomass conversion and harvesting solar power. After two centuries, niobium may finally receive some long overdue recognition. □

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