The Effect of Materials on Time

Donald B. Sullivan

Introduction

We all know that the properties of a material can change with time, but is the inverse possible? How can materials have an effect on time? In the strictest sense, the idea is absurd. However, our ability to keep track of time is clearly dependent on the materials we use to construct our clocks. The performance of many early mechanical clocks depended on the materials of fabrication, and today's high-technology clocks depend no less critically on materials.

My objective in this brief article is to divulge a few materials problems involved in clock technology. Since I do not attempt a comprehensive report, I will undoubtedly leave out some issues that colleagues in the field would consider important.

Who Cares?

Navigation has been a key driving force for the development of accurate timekeeping, at least since the 17th century. While many other important applications require accurate timekeeping (e.g., synchronization for telecommunications and electrical power distribution), I focus on navigation because of its historical significance and its particularly graphic illustration of why clocks have attained such prominence.[1]

Celestial Navigation

I arbitrarily associate the genesis of highly accurate timekeeping with the introduction of the pendulum clock. Galileo Galilei developed the concept for the pendulum clock in the late 16th century, but the first such clock was built by Christian Huygens in 1657. Pendulum clocks quickly eclipsed all earlier methods of mechanical timekeeping, achieving an accuracy of better than one second per day, with the best devices doing even better than one second per month.[2]

However, this performance could not be realized on the high seas since a pendulum clock cannot keep time on an unstable platform. This was unfortunate, because good timekeeping was desperately needed for navigation. World trade was increasing dramatically, and navigation errors were causing growing numbers of mishaps with great losses of life and property. Mariners knew how to determine latitude by observing the elevation of certain celestial bodies, but a means of shipboard timekeeping was needed before such observations could be used to determine longitude.

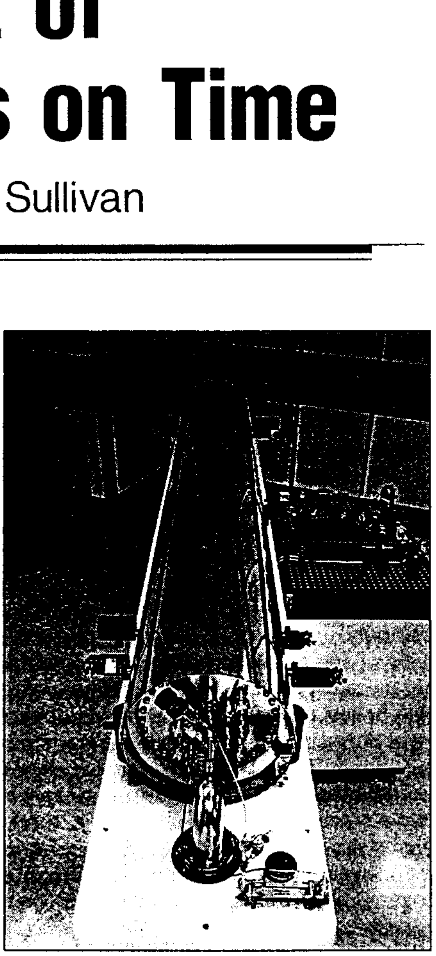

Figure. NIST-7, the U.S. primary atomic clock. This standard contributes significantly to the accuracy of the rate for international time and lends long-term stability to NIST's time scale. This increased stability is needed for large network applications and for tests of scientific theories. The standard also serves as a reference in evaluating the performance of advanced commercial frequency standards. This cesium-beam frequency standard is based on optical state-preparation and state-detection methods as opposed to the magnetic methods used in earlier generations of atomic standards. In this process, atoms are forced by laser radiation into the desired atomic state and then state-detected using a similar laser method. The laser system is on the small table beside the standard. NIST-7 is the world's most accurate atomic standard. It realizes the definition of the second with a fractional uncertainty of 1 × 10^{-14}.

Several governments focused on this issue and offered prizes for solutions. In 1714, Great Britain passed "an act for providing a publick reward for such person or persons as shall discover the longitude at sea." Some 10 years later, John Harrison, a self-taught British clockmaker in his early 30s, learned of this offer. He dedicated the remainder of his life to the pursuit of the £20,000 prize, a huge sum in those days. He ultimately succeeded and managed to collect most of the prize money several years before his death in 1776 at the age of 83. The stories of his long development effort and his difficulty in extracting the prize are well-recounted in two articles.[3,4] Harrison began with a plan to adapt the pendulum-clock concept to a rolling platform, but his prize-winning chronometer was ultimately a well-made, balance-wheel clock. For nearly two centuries following this development, mechanical marine chronometers played a key role in navigation. The innovations incorporated in Harrison's various clocks provide good examples of early attention given to the materials of clock construction.

Satellite Navigation

With the dawn of the satellite age in the 20th century, new opportunities for more accurate navigation arose. Several concepts evolved, but the most successful was the Global Position System (GPS), a Department of Defense (DOD) constellation of orbiting satellites, each of which broadcasts accurate time signals and accurate satellite-position information. With the reception of four such signals traveling at the speed of light from different satellites, the navigator can now determine longitude, latitude, and altitude within a few meters, anywhere on the earth. In reality, DOD has added an encrypted degradation to the system so that civilian users cannot make these determinations nearly as well as military users. Nevertheless, the civilian market for receivers has grown to the multi-billion-dollar level. The system measures distance by measuring the time of flight of signals moving at the speed of light (about 1 m in 3 ns). The demanding timing required by this system depends on atomic clocks. Atomic clocks ride aboard each satellite, with other atomic clocks in the ground stations that control GPS.

Examples of the Role of Materials in Timekeeping

Let us turn now to some examples of how materials have played a role in timekeeping. I ignore some materials considerations of generic concern. For example, I have neglected the strength-to-weight ratio of materials used for gears in mechanical clocks. While important, the issue is generic, and does not serve as a major stumbling block in clock development. This section addresses general considerations of mechanical friction, expansion coefficient, mechanical/electrical loss, and magnetism.

Mechanical Friction

Friction in bearings was a major consideration in the design of early mechanical clocks. It impeded the motion of moving parts in a manner that simply could not be controlled. In the 17th and 18th centuries, good lubricants were unavailable. The clockmaker had to select special bearing materials that minimized frictional losses since such losses had a substantial influence on clock performance. Harrison demonstrated great ingenuity in this respect. He used brass against lignum vitae—a very dense and oily wood—for roller bearings in some of his earliest clocks. Some of his escapements involved knife edges rocking in

Atomic Clocks

Three types of atomic clocks are commonly used today: cesium-beam clocks, rubidium clocks, and hydrogen masers. These devices are often called frequency standards. The cesium-beam clock has intrinsic accuracy since it embodies the definition of the second (the duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium-133 atom). Custom-constructed primary cesium standards such as NIST-7, the United States' primary standard operated by the National Institute of Standards and Technology, are one-of-a-kind standards designed to accurately realize the second. Commercial cesium-beam clocks typically cost about $50,000. Rubidium clocks are simpler and of lower performance, but typically sell for less than 10% of the cost of cesium clocks. Their performance is above that of high-performance quartz clocks. Hydrogen masers are at the high-cost end, typically priced at five times the cost of a cesium clock. While the hydrogen maser does not have the intrinsic accuracy of the cesium-beam clock, it exhibits dramatically superior short-term stability, making it useful in a number of applications. Each of these devices relies on an atomic transition (a resonance) that is very narrow and relatively insensitive to environmental fluctuations (such as changes in magnetic field). However, the way in which each operates is substantially different. The descriptions that follow are meant to provide a general understanding of the three modes of operation.

The traditional cesium standard involves a thermal beam of cesium atoms, generated in a simple oven and terminating in a special detector. The beam, traveling in a high vacuum, goes through a state-selection region that is traditionally a Stern-Gerlach magnet (an inhomogenous magnetic field) where atoms are separated into their different quantum states with only the desired ground-state atoms proceeding down the beam tube. The atoms then enter a resonant cavity where they are subjected to a microwave field that can be tuned in frequency through the cesium atomic resonance (much narrower than the cavity resonance). The atoms then enter a second Stern-Gerlach magnet arranged so that the only atoms allowed to complete the journey to the detector are those that have been forced to the other cesium ground state by the microwave field. No signal is received by the detector unless the microwave frequency is tuned to the cesium resonance. This type of standard is called a passive standard because it simply responds to the external microwave signal. The detector signal is used to servo-control the microwave source to the cesium resonance.

The rubidium standard is also passive. However, it is not typically operated in a beam configuration. Rather, gaseous rubidium is contained within a cell, which is in turn situated within a resonant microwave cavity. A discharge lamp, filtered to transmit light coincident with an optical transition (not the clock resonance) in rubidium, causes transitions to this much higher energy state where the atoms then reradiate photons to return to a lower energy level. Because of the quantum selection rules associated with this optical transition, the rubidium atoms end up in the desired hyperfine atomic state where they can be probed by a microwave signal (about 6.8 GHz) sent from an external source to the cavity. The detection process in this case involves the light transmitted through the cell. As the microwave signal is tuned to the rubidium resonance, rubidium atoms are stimulated to undergo transitions to the other clock state where they once again become available for the optical pumping process. This process absorbs light, so the rubidium resonance is sensed as a decrease in the amplitude of light transmitted through the cell.

The hydrogen maser operates in yet another mode. Most masers are active rather than passive, that is, they need no external signal, but rather oscillate spontaneously. The word "maser" is an acronym for microwave amplification by stimulated emission of radiation and is analogous to the familiar laser. In the maser, hydrogen atoms are state-selected using a magnetic method (as in the cesium standard) and sent into a storage bulb within a microwave cavity that is tuned to the desired hydrogen resonance (about 1.42 GHz). Within the bulb, some atoms spontaneously drop to a lower state, emitting photons that in turn stimulate other atoms to make the same transition. Additional atoms are continuously supplied to the bulb, and a self-sustaining oscillation builds up. The microwave cavity plays an important role in containing the emitted photons so that they are not too quickly lost to the surroundings.

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polished grooves which were cut in small glass plates, and in his successful marine chronometer, he made good use of jeweled bearings. While he did not invent jeweled bearings, he is believed to be the first to have made extensive use of them. Friction in bearings arises in other contexts but was a particularly difficult problem in this early phase of clock development. A good selection of materials was critical.

Expansion Coefficient

The mechanical stability of early clocks directly influenced their performance. For example, since a change in temperature altered the length of a pendulum, thus altering the clock's rate, Harrison and others developed schemes to compensate for such expansion. Harrison, after measuring the expansion coefficients of steel and brass, combined five steel and four brass rods in a folded geometry that kept the pendulum length nearly constant as temperature changed. Later pendulum clocks incorporated pendulum alloys of exceedingly low expansion coefficient. In his later chronometers, Harrison used a bimetallic strip of brass and steel to control the position of one end of the balance-wheel spring. He adjusted the bimetallic strip so that the frequency of oscillation of the balance wheel would remain nearly constant as the temperature varied. Still others recognized that the moment of inertia of the balance wheel was also affected by dimensional (and thus temperature) change.

While modern timekeeping has moved well beyond mechanical clocks, the need for dimensional stability has remained. The frequency of quartz-resonator-controlled clocks and oscillators is temperature-dependent at least partly because temperature-induced expansion changes the size of the resonator. In addition, quartz resonators must be mechanically mounted to minimize stress in the very thin crystals. This requires careful attention to the materials and methods of suspension. Through expansion coefficient, temperature change can induce a change in crystal stress, and thus indirectly produce a change in frequency.[5]

Expansion coefficient also concerns designers of atomic clocks. These clocks typically involve an atomic resonance interrogated by a microwave field generated within a resonant cavity. The dimensions of the microwave cavity must remain stable lest a change in that resonance produce any unwanted pulling of the critical atomic resonance.[6] Temperature is usually controlled to assure the required dimensional stability, but better results are obtained if care is first exercised in selecting the materials of construction for the cavity. The required dimensional control can be very demanding. The frequency uncertainty of the best cesium-beam atomic clocks can be as small as 10^{-14}, and the uncompensated drift rate in a hydrogen maser (another type of atomic clock) can be as low as 10^{-15} per day. In the best hydrogen masers, the drift in cavity dimensions inferred from frequency drift is approximately 10^{-11} m per day. Since this drift persists indefinitely and is not associated with temperature change, researchers conclude that it results from long-term aging in the material, that is, some type of gradual reordering of atoms in the material. Atomic clocks provide tremendous measurement resolution for such effects.

To reduce their physical size, some hydrogen masers incorporate a material of high dielectric constant within the cavity. In these devices, stability of not only the dimensions of the cavity but also the dielectric constant are clearly limiting considerations. Drift in the output of such hydrogen masers is often attributed to drift in the resonant frequency of the cavity and thus drift in the effective electrical dimensions of the cavity.

Mechanical and Electrical Damping

I have shown that a key device of a good clock generates a constant frequency (a frequency standard or stable oscillator). A frequency standard is converted into a clock when we add a mechanism for keeping track of the ticks. I have covered three frequency standards: the pendulum, the quartz resonator, and the atomic resonator. The parameter used as a figure of merit for such devices is the quality factor or simply Q, which is a measure of the ratio of the energy stored to the energy lost per cycle of oscillation. The higher the Q, the more nearly the device stays on its resonant frequency. In other words, the frequency width of the resonance decreases as Q increases. Here the properties of materials again become important. The losses that limit the Q (i.e., damp the resonance) are often intrinsic to the materials of construction. A better material can produce a higher Q and thus hopefully a better clock. Let us consider a few cases.

Quartz Resonators

While many efforts have been made to find better materials for acoustic-wave resonators, quartz resonators still dominate the market. One promising new material (under development now) is langasite ($La_3Ga_5SiO_{14}$). This material falls into the same symmetry class as α-quartz. The implication is clear. Quartz's unique set of properties make it ideally suited for this application, so searches for new materials focus on quartzlike materials.[7]

The typical bulk-acoustic-wave (BAW) resonator, operating in a shear resonant mode, is the most common form of high-performance resonator used. However, interest is growing in surface-acoustic-wave (SAW) devices. Quartz resonators control the operation of devices ranging from wrist watches to sophisticated electronic instrumentation. Since timing is of importance in so many electronic applications, quartz technology is ubiquitous in electronics. Production of quartz oscillators is estimated to be about 2×10^9 units per year. Since quartz resonators are small and inexpensive and require very little power, they are the device of choice if they can meet the performance requirements.[8]

To produce a BAW resonator, a slab of appropriate geometry is sliced from a larger crystal at a particular angle relative to the crystal lattice. Temperature dependence of the resultant device's frequency (as well as other characteristics) depends critically on this angle. The temperature coefficient typically changes sign at a temperature dependent on angle. Thus, operation at the turnover point results in a minimal temperature coefficient. As an example, quartz oscillators for many wrist watches are cut so that the turnover temperature is near body temperature. This obviously results in better timekeeping.

Attenuation of acoustic waves in the quartz crystal is very important in determining the behavior of devices. Losses in the crystal are treated as the imaginary part of the elastic stiffness. Acoustic velocity is no less important. Together with physical size, acoustic velocity determines the frequency of oscillation for a device, and environmental fluctuations affecting acoustic velocity thus translate into frequency fluctuations. Full characterization also requires knowledge of the piezoelectric and dielectric properties of the material.

Crystals used in the early days of quartz-resonator technology were of naturally occurring quartz, and performance was highly dependent on the exact source of the quartz material.[9] Natural crystals ultimately gave way to synthetically grown crystals resulting in a substantial decrease in the variability of results. Yet materials problems and variability in performance still remain. Nonuniformly distributed interstitial hydrogen and mobile impurities and defects affect acoustic velocity as well as Q, and thus the performance of devices.

Despite steady advances in understanding the materials problems with resonators, researchers have recently found that higher Q, while a necessary condition for better device performance, is not necessarily sufficient. They have noted the presence of flicker noise (noise that is proportional to the reciprocal of frequency, that is, that increases with decreasing frequency) which obviously arises within the quartz or metal-electrode material but has not yet been well-correlated with any material parameter. One speculation is that this noise is a result of random fluctuations in the states of impurities or defects within the crystal.[10] Another possibility is that the flicker noise is caused by quantum interactions.[11] Yet experiments designed to test these hypotheses have produced inconsistent results. Most likely several mechanisms are involved, so the experimental conditions are not under full control. The materials problems continue to be an area of investigation.

Resonators for Atomic Clocks

The reference resonance by which atomic clocks are controlled is a property of the atoms used in the clock. This is typically a subject of interest to the atomic physicist, not the materials scientist. Nonetheless, electronic resonators (typically in the microwave region) play a major role in atomic clocks, and materials influence the characteristics of the electronic resonator. The materials problems here are generally not as profound as those in quartz resonators, but clearly designers of atomic clocks must pay careful attention to the materials used.

Wall Coatings within Resonators

The two previous sections considered losses in macroscopic resonators (quartz resonators and microwave cavities). Materials also directly affect the atoms' resonance during their interactions with the wall coatings of storage bulbs within the resonators of hydrogen masers.[12] The walls of the storage bulb play a key role in determining the performance of the maser. In these masers, hydrogen atoms are state-selected outside the resonator using magnetic methods. They are then sent into a containment region, usually a vitreous silica bulb, within the resonator.

Ideal performance is obtained if the atom can be contained in the bulb for long periods with little or no perturbation of its atomic, electron-spin state. Since the atom cannot be prevented from striking the walls of the bulb, the bulb is coated with a material that minimally disturbs the atomic state. Several types of Teflon, such as polytetrafluoroethylene (PTFE) and fluorinated ethylene propylene (FEP), have worked well as wall coatings. The strength of the fluorine-carbon bond and the inert character of carbon seem to produce a stable coating with strong properties. When hydrogen strikes such a coated wall, its atomic state is perturbed, but the perturbation can range from positive to negative amounts, so the net perturbation might in some cases average to 0. The atom as it nears the wall experiences an attractive van der Waals force. On very close approach, the force becomes strongly repulsive. Because the electrons of the surface atoms are strongly bound, the hydrogen atom sees only this weak attraction and then strong repulsion. The ideal situation seems to be a simple, hard-sphere, van der Waals interaction. Clearly, the presence of nonideal impurities, particularly magnetic impurities, in the wall coating can be disastrous since any spin-exchange interaction completely alters the atomic state of the hydrogen.

While scientists have a rough understanding of the physics of the wall interaction, the coating of walls in masers remains a murky process. Through trial and error, successful recipes have been developed, but researchers do not have good diagnostic methods for characterizing the wall surface nor full control of the coating process.

Magnetism

Another consideration in high-performance clocks is their sensitivity to magnetic field. Stable, high-permeability magnetic shields are essential in all high-performance clocks. The best clocks use three and even four layers of shielding. The clock designer must also avoid the use of magnetic materials, even weakly magnetic materials (such as some brasses), in certain regions in the clock. The requirements are straightforward, but materials selection is critical.

Magnets also manipulate and detect the states of atoms in certain atomic clocks. Magnetic-state selection is used in hydrogen masers, and conventional cesium-beam standards use magnetic methods for both state selection and state detection. Permanent magnets designed to have strong magnetic gradients generate differing forces on atoms that are in different spin states. These forces enable separation of atomic states in a manner somewhat analogous to mass spectrometry. The long-term behavior of these types of clocks depends on the quality and stability of this state-separation process, thus requiring careful selection of the magnetic material.

Directions for the Future

Quartz-controlled clocks undoubtedly will continue to dominate in numbers. Gradual advances in acoustic-wave resonators will most likely accompany advances in the understanding of the quartz material and possibly the introduction of new materials. Atomic clock technology, on the other hand, is undergoing major change. Over the last decade, physicists have learned how to use lasers to control the motions and atomic states of atoms and ions, affecting the stability and accuracy of timekeeping. Immense improvements in atomic clocks can be expected over the next several decades. Since these new clocks are still in the research laboratory, their materials requirements are not completely clear, but these requirements are likely to fall into the categories described here.

Acknowledgments

Except for the gravitational force associated with proximity to a large mass, materials do not directly affect the passage of time. Yet materials play a role in our ability to keep time. Despite this, I could not pass up the title, "The Effect of Materials on Time," suggested by Elton Kaufmann, Chair of the *MRS Bulletin* Editorial Boards. I would like to thank him for encouraging me to write this article. I also thank my colleagues, Tom Parker and Fred Walls of the National Institute of Standards and Technology in Boulder, Colorado, and Bob Vessott of the Harvard Smithsonian Center for Astrophysics in Cambridge, Massachusetts, for assistance and comments.

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