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Tutorial

# Effect of temperature on beam damage of asbestos fibers in the transmission electron microscope (TEM) at 100 kV

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ABSTRACT

Damage to asbestos fibers by the transmission electron microscope (TEM) electron beam is a known limitation of this powerful method of analysis. Although it is often considered only in terms of loss of crystallinity, recent studies have shown that the damage may also change the elemental composition of fibers, thus causing significant identification errors. In this study, the main objective was to assess whether temperature is a factor influencing damage to asbestos fibers and, if so, how it can be used to minimize damage. It was found that lowering the temperature to 123 K can inhibit, for a given time, the manifestation of the damage. The significant decrease of atom diffusion at low temperature momentarily prevents mass loss, greatly reducing the possibility of misidentification of anthophyllite asbestos fibers. The results obtained in this study strongly suggest that the predominant mechanism damage is probably related to the induced-electric-field model relegating radiolysis to the status of a subsidiary damage mechanism.



## 1. Introduction

Asbestos is a commercial term applied to a group of naturally occurring, inorganic and highly fibrous silicate minerals that have grown in a specific crystal habit and exhibit characteristics of flexibility, high tensile strength, electrical resistance, and resistance to heat and chemical degradation. Six asbestiform minerals are currently regulated as asbestos by most health regulations worldwide; chrysotile, from the serpentine mineral group, and five minerals from the amphibole group: crocidolite (riebeckite asbestos), amosite (cummingtonite-grunerite asbestos), anthophyllite asbestos, tremolite asbestos, and actinolite asbestos. Asbestos has been mined because of its advantageous properties and increasingly used in many commercial applications since the second half of the 19th century until reaching a maximum global production in 1977 of $4.8 \times 10^6$ tons (Virta 2002). To a lesser extent, its use for different purposes is very old; evidence was found in Finland that asbestos fibers were incorporated in pottery as far back as 2500 BCE. Other uses of asbestos, such as in oil lamp wicks or cremation cloth, are reported in ancient writings.

Asbestos is also commonly associated with potential disease, with the first cases of asbestos-related disease being reported in the early 1900s in France and the United Kingdom (Murray 1990). Reaction was slow to manifest even though more and more cases were identified throughout the century and research on these diseases was becoming better documented (Cooke 1924; Baron 2001; Castleman and Berger 2005). It was only in the 1970s that the health effects of asbestos became a real concern; at this point its industrial use began to decline as many epidemiological studies were conducted on different aspects of asbestos hazards. Nowadays it is well recognized that asbestos exposure can cause several irreversible diseases such as asbestosis, lung cancer or mesothelioma (Dodson and Hammar, 2011). Although its use has been almost entirely phased out in most industrialized countries, asbestos is still frequently encountered in buildings or road constructions, mainly as insulation material or asbestos cement, and in a surprisingly wide variety of building materials, for example, vinyl floor tiles. Since asbestos abatement sites are numerous, worker exposition is strictly controlled and regulated. The toxicity of asbestos fibers is generally determined based on three main factors: fiber dose, fiber dimension, and fiber durability in lungs (Lippmann, 1990). According to the regulations applied, the analytical technique may be required to determine the morphology of the fibers, their exact nature (by chemical and crystallographic analysis) and

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concentrations in various media such as air, bulk materials, water or lung tissue. Optical microscopy is the experimental technique most commonly used for asbestos analysis because it offers significant advantages such as speed and low cost, but when a complete and accurate analysis is needed, transmission electron microscopy (TEM) is the technique to use. While this analytical technique is quite complex, time-consuming and costly, it is one of the only ones to get as much information from a single analysis. It measures the morphological criteria for each fiber with an image resolution of easily less than one nanometer, which is particularly useful for small-sized fibers such as are often found in floor tiles or lung tissue. It allows complete chemical analysis using energy-dispersive X-ray spectroscopy (EDS) by identifying all the elements present in the fibers and their respective proportions, and also provides important crystallographic information using electron diffraction patterns obtained in selected area electron diffraction (SAED). Combining all this information allows complete characterization of asbestos fibers and thus a highly reliable identification.

Different standard procedures are available for asbestos analysis by TEM. These are often very similar to each other and describe in some detail the procedure for the analysis (EPA, 1993; ISO, 1995). These methods also have certain limitations and disadvantages, one of which is the sensitivity of the asbestos fibers to the electron beam. Damage due to the electron beam in the TEM is a well-known phenomenon and fairly well understood for some types of materials or samples. The signals due to elastic and inelastic interactions of electrons with the sample are used to obtain information on the physical, chemical and crystallographic properties of the sample; this is what makes this analytical technique so complete. The same types of interactions, however, can lead to damage in the sample and thus alter the properties that are to be determined. To avoid damage to the sample, the experimental conditions used vary depending on the dominant damage mechanisms, so it is very relevant to attempt to understand them.

There are many different mechanisms of radiation damage, each of which has specific effects on the sample. For some types of materials or given experimental conditions, it may be possible to know which damage mechanisms are most likely to be active. This is unfortunately not so simple with other materials, including asbestos, where the presence of several damage mechanisms is suspected.

The damage can have various impacts on the sample, including changes in the structure or chemical composition. In the case of asbestos fibers, both are observed. Amorphization of the crystal structure of the fiber is one observable indication of electron beam damage: both the crystallographic planes and the diffraction contrast disappear. Under certain illumination conditions, it is also possible to observe a change in the chemical composition as measured by EDS analysis. This second indication of damage is more problematic than a loss of local crystallinity, since it can easily go undetected and thus lead to misidentification of the fiber. It is therefore particularly important to better understand which damage mechanisms are operating and how they work in order to reduce their impact and increase the reliability of the analysis.

Generally, damage mechanisms are classified in two categories related to the nature of the interaction leading to damage. The first is damage resulting from elastic scattering, where following an electron-nucleus interaction, the electron transfers energy to the atom. If the transferred energy exceeds the threshold energy of atomic sputtering or atomic displacement, it results in damage. These interactions are called knock-on processes and may affect all types of samples when the energy of the electron beam is sufficient, and are usually predominant in conductive samples.

The other type of damage mechanisms are ionization damage or radiolytic damage, which are processes arising from inelastic interactions between electrons. Radiolytic damage occurs when energy is transferred from an electron beam to an atomic electron in the specimen, increasing the energy of the electrons from the ground state to an excited state. For this excitation to cause damage in the sample, it needs to be converted to kinetic energy and momentum of atomic nuclei and the excitation must be localized long enough for the atom to respond mechanically. When these two conditions are satisfied, which is often the case for insulating materials like asbestos, the bonding instabilities may lead to specimen damage.

Radiolysis is the main mechanism by which radiolytic damage occurs. The ionization causes the formation of radicals by bond breakage. It is also generally regarded as the predominant type of mechanism in silicate crystals.

A third possibility is electrostatic charging. This interaction, which mainly occurs in insulating materials with the ejection of Auger and secondary electrons, involves both elastic and inelastic scattering. When surrounding electrons cannot compensate quickly enough for the missing ones, a positive potential is created in the illuminated area which may result in a lateral migration of cations and anions, drawing anions into the irradiated area and expelling cations. This mechanism is also responsible for other observed phenomena, such as hole drilling and image distortion or blurring (Cazaux, 1995).

It is not easy to determine in what proportion these three mechanisms affect specimen damage for our material, but it is likely that all three are present. Since experiments were conducted for this study at a relatively low accelerating voltage (100 kV) on an insulating material, it can be assumed that knock-on damage is limited compared to radiolysis and electrostatic charging (Inui et al., 1990); however, it cannot be overlooked (Crozier et al., 1990; Ugurlu et al., 2011).

Several strategies have been proposed for purposes of reducing damage on some types of samples for analysis by TEM, with varying efficiency. One of the most common ways, mainly used for organic samples, is to lower the sample temperature during the analysis.

Several studies have shown that lowering the temperature of the sample made it possible to significantly increase the critical electronic dose at which the diffraction spots become completely invisible and to significantly reduce the loss of mass (Hall and Gupta 1974; Knapek and Dubochet, 1980; International Experimental Study Group 1986; Chinte et al., 2007).

Knock-on processes are not influenced by temperature because it has no effect on the momentum transfer to a nucleus (Egerton et al., 2004); radiolysis, on the other hand, is known to be temperature dependent to some extent (Hobbs 1975; Egerton et al., 2004). For radiolytic bond breakage to lead to specimen damage, the excitation energy has to be converted into momentum. When this occurs, atomic displacement can be achieved either by Coulomb repulsion, by atomic vibration or both. Atomic vibration is strongly temperature dependent and therefore radiolysis damage is generally influenced by temperature variations to the extent that the transfer of momentum by atomic vibration is present (Hobbs 1990; Jiang, 2016b). It may also be possible to reduce charging effects by lowering the temperature since the mobility of ions increases with temperature.

While it is commonly accepted that lowering the temperature reduces the beam damage sensitivity of a sample susceptible to radiolysis, a great difference is observed in the damage decrease factors reported (between 3 and 100) (Knapek and Dubochet, 1980; International Experimental Study Group 1986; Egerton et al., 2004) and the optimal temperature to use (Chinte et al., 2007; Meents et al., 2007). This reduction in damage due to cryogenics, however, is only temporary: when the sample returns to room temperature, the atoms dislodged as a result of the chemical bond become mobile again and can easily leave the previously illuminated region (Egerton 1980; Egerton 2013).