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文化財における金属周辺木材の白色現象：
特徴と発生機構

Whitening phenomenon of wood adjacent to metal components of cultural properties:
Characterisation and occurrence mechanism

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1. Introduction

The whitening phenomenon of wood could adversely affect the appearance and aesthetic value, and cause worries about the durability of the historic wooden cultural properties

Generally, the whitening phenomenon of wood occurred in historic wooden architectures would likely be attributed to the external factors: White-rot fungi[1], UV and visible irradiations[2]. While in recent researches of the whitening phenomenon occurred in the wood in contact with base-stones, the whitening phenomenon of wood has been ascribed to inorganic compound, especially gypsum[3]. On the other hand, the whitening phenomenon of wood is also observed in the area adjacent to metal components in the case of historic architectures (Fig.1).

The metal components of cultural properties are irreplaceable parts for the consideration of preserving the integrity of original materials, as well as the historic and aesthetic values. On the view of preventative conservation, it is essential 1) to distinguish the whitening phenomenon of wood adjacent to metal components from the other types of the whitening phenomenon, 2) figure out the occurrence mechanism, conditions and affecting factors, 3) develop suitable preventive conservation strategies correspond to different types of the whitening phenomenon. To realise this objective, the following studies were conducted in the research. First of all, the phenomenon was characterised by scientific case studies. On the base of this result, a hypothesis of the occurrence mechanism was proposed. The hypothesised mechanism and the related affecting factor were evidenced and improved through model experiments with fresh wood.

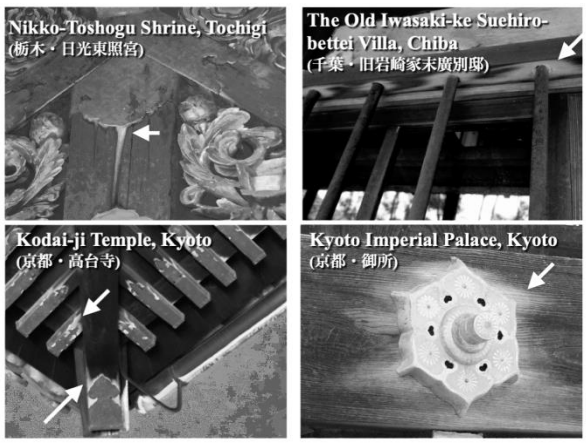
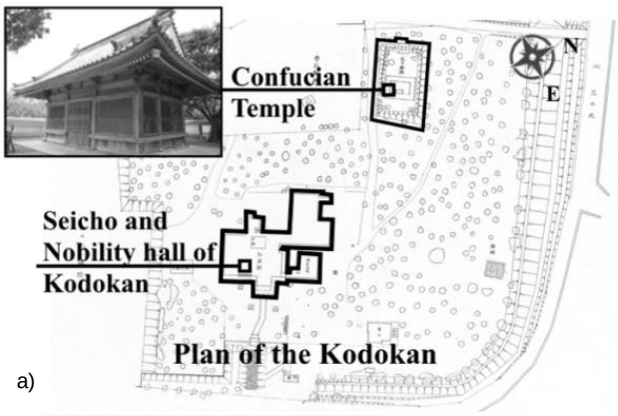
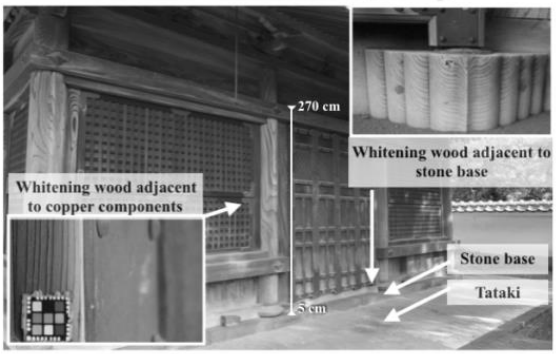


Fig. 1 The whitening phenomenon of wood adjacent to metal components, in the case of Japanese historic architectures.

2. Characterisation for the whitening phenomenon of wood adjacent to metal: in the case of the Confucian Temple of the Kodokan of Mito Domain



a)



b)

Fig. 2 a) Plan of the Kodokan(“弘道館修理工事報告書”1963) and the photograph of the Confucian Temple((施設紹介. 弘道館公園. http://www.koen.pref.ibaraki.jp/park/kodokan04.html. [Accessed 27 Sep., 2015]); b) the 2 different types of whitening phenomenon of wood in the Confucian Temple.

世界遺産学研究 No. 6 (2018)
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This part of research attempted to distinguish the whitening phenomenon of wood adjacent to the metal component from the other types of the whitening phenomenon at different locations in the case of the Confucian Temple of the Kodokan of Mito Domain, through *in situ* elemental analysis, colourimetric measurements and microscopic observation (Fig.2).

As the results, it is proved that:

XRF analysis could be an effective method to figure out the elemental characteristics of wooden constructions with the different types of whitening phenomenon. Results of elemental distribution investigation for exterior side present that the whitening phenomenon in wooden constructions lower than 70 cm height is predominantly affected by Ca, Fe, Cl, S elements; the whitening phenomenon of wood adjacent to copper components is predominantly affected by Cu element (Fig.3).

No matter in "Ca affected" or "Cu affected" whitening phenomenon of wood, both the "non-particle-attached" type and the "particle-attached" type of whitening phenomenon are observed.

The FTIR analysis for the Nageshi samples confirms the simultaneous chemical changes of wood structural constituents in "non-particle-attached" whitening phenomenon of wood once adjacent to copper components.

The connection between Cu content and whiteness degree has been confirmed in the case of vertical wooden window frames in situ. In contrast, in the case of the Nageshi, wood with significant Cu content while lower whiteness degree is also verified.

In conclusion, the existence of Cu in the wood will not necessarily lead to whitening colouration change of wood. It is worth to figure out how the Cu content affects wood tissues, and if the affection would result in the "non-particle-attached" type and the "particle-attached" type of whitening phenomenon in Cu affected wood.

3. Characterisation for the whitening phenomenon of wood adjacent to metal: in the case of the Old Iwasaki-ke Suehiro-bettei Villa

On the results of the previous investigation, further field investigation for the Old Iwasaki-ke Suehiro-bettei Villa were conducted to identify the chemical composition of the additional whitish particles among wood tissues, and figure out the chemical features of wood with the

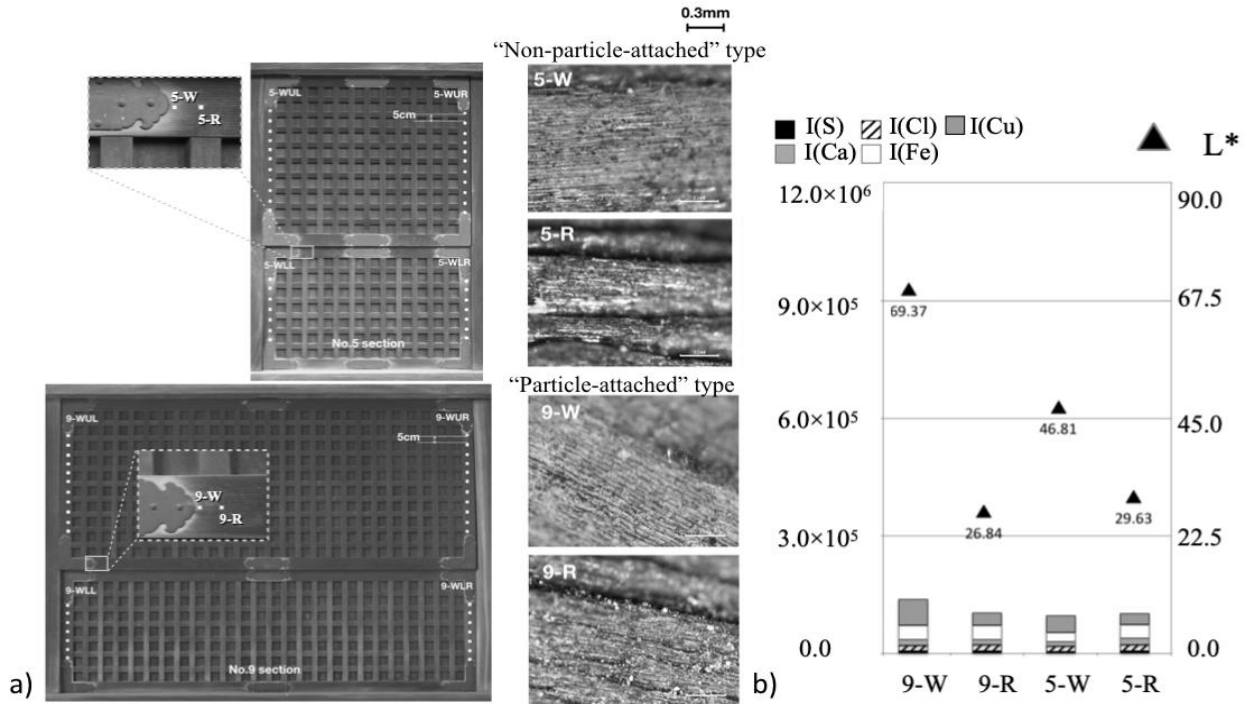

Fig. 3 The wood with whitening phenomenon adjacent to copper components(radical section of wood) in the case of the Confucian Temple of the Kodokan of Mito Domain: a) location of the whitening points adjacent to metal (5-W,9-W) and reference points distant from metal(5-R,9-R), and the microscopic photographs of which; b) the staked column graph of I(S), I(Cl), I(Ca), I(Fe), I(Cu) (detected intensity of element) obtained by XRF analysis with L* values (whiteness degree in the 1976 CIE L*a*b* colourimetric system).

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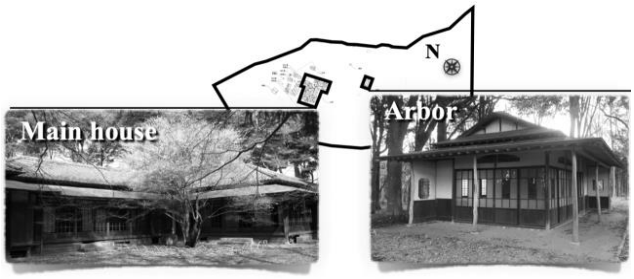

Fig. 4 The Old Iwasaki-ke Suehiro-bettei Villa

whitening phenomenon for the better understanding.

As the results, the scientific investigation confirms the various surface features of wood with similar whitening phenomenon affected by different types of metal.

A "non-particle-attached" whitening point is confirmed in wood adjacent to Cu-Zn alloy components at interior location. In this case, a simultaneously degradation of wood structural constituents is verified with FTIR analysis.

Besides, additional different inorganic compounds are identified in the other investigated whitening points, no matter the locations and the functions of the wood components:

- Jarosite [$KFe_3(SO_4)_2(OH)_6$] in the vicinity of iron nails;
- Zinc oxalate hydrate ($ZnC_2O_4•2H_2O$) in the vicinity of Cu-Zn alloy components;
- Moolooite ($CuC_2O_4•xH_2O$) in the vicinity of copper nails.

The SEM-EPMA observation presents the existing state of inorganic compounds may be fine particles among wood tissues (Fig.5).

The existence of oxalate ion content is confirmed in wood. In the wood adjacent to the Cu and Cu-Zn alloy components, the oxalate ion may generate from the Cu/Zn affected degradation of wood structural constituents, subsequently combined with the metal ion to form the additional oxalate particles.

Overall, it could propose that the whitening phenomenon of wood adjacent to metal may relate to the chemical changes of wood structural constituents for the case of "non-particle-attached" whitening phenomenon, both chemical changes and formation of certain inorganic compounds in wood tissues for the case of "particle-attached" whitening phenomenon.

4. Quantification of ion content for the whitening phenomenon of wood adjacent to metal: with nondestructive investigation method

On the results of the field investigation, it is speculated that the formation of the metal oxalate compounds could be ascribed to the combination of mobile zinc and oxalate ions in wood. The quantitation of zinc and oxalate ions in wood with the whitening phenomenon may display significant characteristics and provide valuable information to discuss the occurrence mechanism for this type of whitening phenomenon. In order to realise scientific investigations for more extensive cases without damages in sampling procedures, a new nondestructive method using filter paper was developed exclusively for cultural properties.

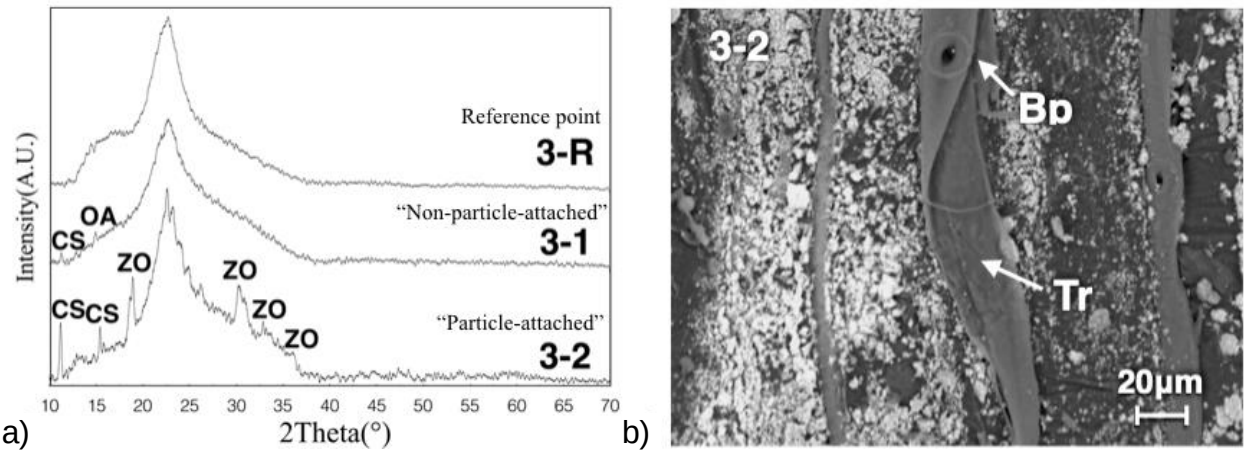

Fig. 5 The whitening points adjacent to metal (3-1, 3-2) and reference point distant to metal (3-R) in the case of the Old Iwasaki-ke Suehiro-bettei Villa, a) the spectra of XRD analysis, CS = calcium sulfite, OA = oxalic acid, ZO= zinc oxalate dehydrate ($ZnC_2O_4•2H_2O$), c) the SEM-BSE image of the 3-2 point with attached particles; the brighter tone of particles represent greater average atomic numbers than which in wood tissues, Tr: tracheid, Bp: bordered pit.

世界遺産学研究 No. 6 (2018)
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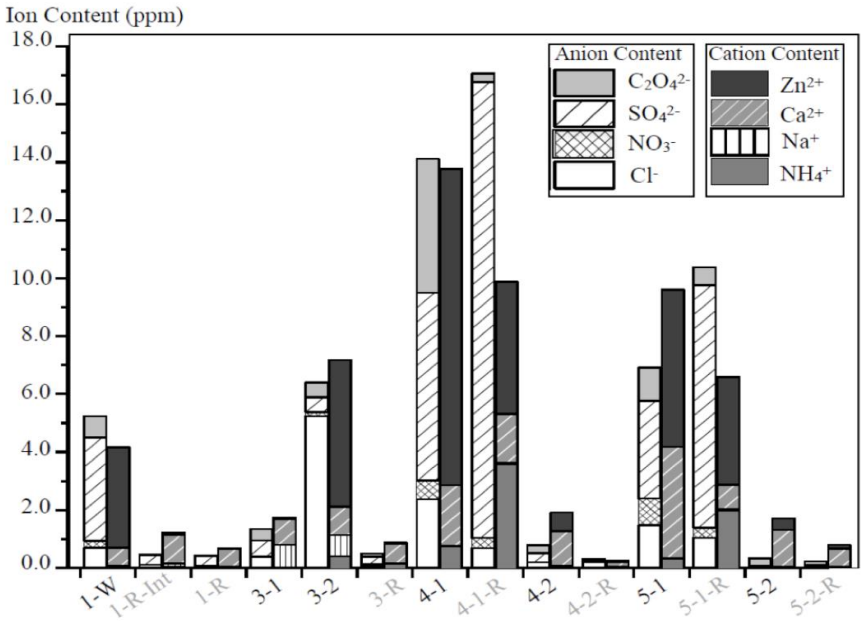

Fig. 6 The stacked column graphs of anion content and cation content in the case of samples from No. 1, 3, 4, 5 investigate location which are points adjacent to Cu-Zn alloy components(1-W, 3-1,3-2, 4-1, 4-2, 5-1, 5-2) and the corresponding reference points(1-R-Int, 1-R, 3-R, 4-1-R, 4-2-R, 5-1-R, 5-2-R).

The method was designed with following procedures:

1) Prepare clean filter papers: filter paper pieces with size as 10×10 mm^2;

2) Put prepared filter papers on the surfaces of wood samples and drop 5ul distilled water on the filter paper;

3) Retrieve the naturally dried filter papers, and then soak each piece into 5 ml distilled water for 48 hs;

4) Analyzing the water extraction of filter papers by IC analysis.

The results of the practice on the Old Iwasaki-ke Suehiro-bettei Villa displays the most significant $C_2O_4^{2-}$ and Zn^{2+} ion contents in the whitening wood adjacent to the metal component of higher locations(Fig. 6). The eaves may shelter these locations from some influences of environmental factors to ensure the accumulation of ion contents and the metal oxalate precipitations.

5. Artificial degradation of Cu and Zn affected wood: occurrence mechanism of the phenomenon

The scientific investigations of previous sections characterised the surface features of the whitening phenomenon of wood adjacent to metal components. Based on these results, a hypothesis is proposed to explain the occurrence of the phenomenon adjacent to Cu and Cu alloyed components: 1) the metal ions in wood, which migrate from metal components during the process of corrosion, catalyse the chemical changes of wood chemical components; 2) the oxalic acid is generated as the product of the chemical changes; 3) the combination of oxalate ion and metal ions in wood would result in precipitation of metal oxalate compound particles among wood tissues[4]. The degradation of wood structural constituents may result in the “non-particle-attached” type whitening phenomenon of wood; the growth and accumulation of the particles will ultimately result in the “particle-attached” type whitening phenomenon of wood. However, the exact formation mechanism of the additional inorganic compounds in wood has not been specified yet, and it is not clear how would the formation processes affect the surface colouration, internal properties, durability and values of wooden cultural properties.

Therefore, a model experiment was performed with artificial degradation of metal affected fresh wood, aimed to provide more basic information of whitening phenomenon adjacent to the copper alloyed component for future conservation activities. The Cu and Zn elements are the most general affecting metal elements of copper alloyed components in the case of cultural properties. Hence, these two elements were selected in this experiment. The changes of the fresh wood samples were evaluated through monitoring: 1) the formation and growth process of oxalate particles, 2) whitening

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colouration change of the surface 3) chemical changes; 4) the mechanical performance.

（1）Experiment design

In this part of the research, affection of Cu and Zn content toward wood, and the formation of metal oxalate compounds in which were focused on. It was decided to perform artificial degradation of wood samples with different Cu/Zn contents under the same condition of 60°C and RH 90%(relative humidity)[5], and evaluate the degradation performance every 30 days.

The recent Sugi and Keyaki were prepared as plate and wood meal samples for monitoring changes of chemical and mechanical features respectively.

（2）Materials

The healthy recent wood of Sugi (softwood, Japanese cedar) and Keyaki (hard wood, Japanese Zelkova) were cut into rectangular plates and crushed into meal with particle sizes of 177-250 um for evaluating different properties.

The wood plate and meal samples affected by Cu/Zn with different contents were prepared by soaking wood plates respectively in $ZnCl_2$ and $CuCl_2$ solutions with 3 different levels of concentrations.

（3）Methods

The chemical changes were evaluated in the combination of FTIR analysis and water extraction analysis included IC analysis for anion contents and High-performance liquid chromatography (HPLC) analysis for monosaccharide contents with wood meal samples.

For the wood plate samples, the Colorimetric measurements, SEM-EPMA analysis was performed to monitor the colorimetric changes and formation process of metal oxalate particles. The mechanical properties were evaluated by flexural vibration test under 25°C and RH 60% condition.

（4）Results

The affection of metal content on degradation performances of wood is evidenced after the 90 days exposure under the 60°C and RH 90% conditions.

Relatively higher decomposition product contents (formate and oxalate ion content, monosaccharide content) and more significant spectral changes of FTIR analysis are confirmed in the case of the samples with Zn/Cu content. For the case with the same kind of metal content, higher content present more significant affection on the degradation of wood. The Cu element always presents more significant affections than Zn element under the same level of content in wood.

The high correlation coefficients of oxalate ion content with different monosaccharide contents are evidenced depending on wood species (Table 1). The monosaccharide contents are generated from

Table 1 The Pearson correlation coefficient(r) of oxalate ion content with monosaccharide contents

Content	r	
	Keyaki	Sugi
Arabinose	0.41	0.41
Galactose	0.66	**0.97**
Glucose	**0.87**	**0.83**
Xylose	**0.86**	**0.96**
Mannose	-0.07	**0.92**

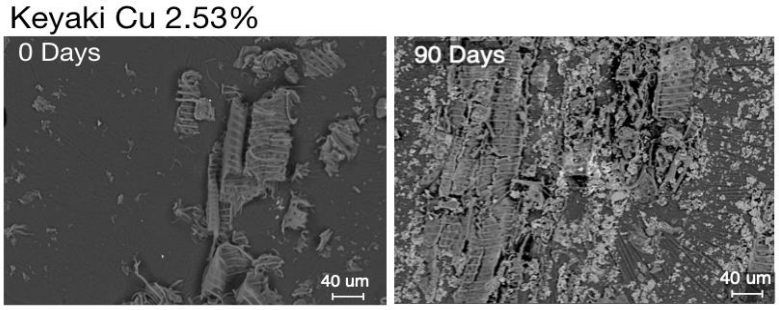

Fig. 7 The SEM-BSE image of Keyaki samples with 2.53% Cu content. The scattered particles with brighter tone are observed among wood tissues after 90 days exposure.

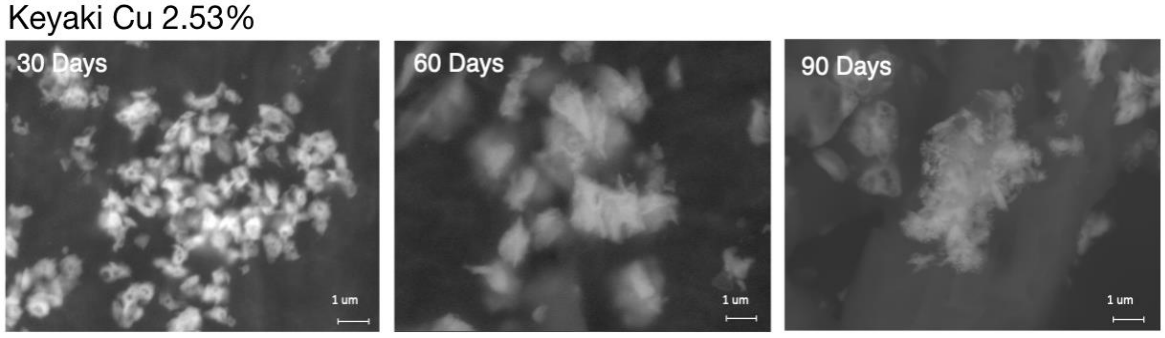

Fig. 8 The high magnification SEM-BSE images of exposed samples with the highest Cu content. The sizes of particles increased with the increase of exposure time.

世界遺産学研究 No. 6 (2018)
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polysaccharide in wood [6], including cellulose and hemicellulose constituents. The decays of bands assigned to cellulose and hemicellulose are also verified in FTIR analysis, along with the appearance of bands belong to the metal oxalate compound, in the samples with high Cu content. It is implicated the oxalate content in wood may result from the depolymerisation of polysaccharide content in wood.

Amounts of additional particles among wood tissues of samples with high Cu content are confirmed with the SEM observation. On the results of FTIR analysis, EPMA qualitative and mapping analysis, it is speculated that the Cu oxalate compounds is exist as fine particles among wood tissues (Fig. 7). Under the observation with high magnification, the particles appear as aggregations of flake-like crystals with the sizes increased with the increase of exposure time (Fig. 8).

The more significant decrease in mechanical properties is also confirmed in the case of samples with high Cu content (Fig. 9). However no visible whitening colouration changes could be confirmed, whether in particle formed or non-particle formed samples.

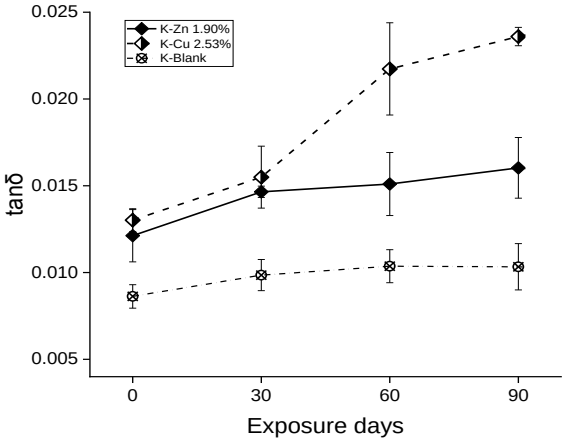

Fig. 9 The tanδ values obtained by the Flexural vibration test of Keyaki samples with 0%, 1.90% Zn, 2.53% Cu content. The increase of tanδ may imply the occurrences of some internal decomposition or breakdown of wood compositions.

6. Conclusion

The 2 patterns of whitening phenomenon adjacent to metal are confirmed both in the Confucian Temple of the Kodokan and the Old Iwasaki-ke Suehiro-bettei Villa, which are "non-particle-attached" type and "particle-attached" type. In "non-particle-attached" type whitening phenomenon, simultaneous decay of the three wood cell wall structural constituents is verified. For the "particle-attached" type whitening phenomenon, the fine particles are identified as Jarosite [$KFe_3(SO_4)_2(OH)_6$] in the vicinity of iron nails; Zinc oxalate hydrate ($ZnC_2O_4 \bullet 2H_2O$) in the vicinity of Cu-Zn alloy components; Moolooite ($CuC_2O_4 \bullet xH_2O$) in the vicinity of copper nails.

The existence of Zn/Cu content could accelerate the degradation of wood chemical constituents, which produce oxalic acid in wood. Fine particles of metal oxalate compound would occur under high Cu content in wood. However, the degradation with products of oxalic acid and the occurrence of metal oxalate particles may not directly lead to whitening colouration change of wood.

On the results of this research, the following prospective are proposed:

1) The accumulated oxalate content in wood could be utilised to evaluate the degradation degree of wood nondestructively, on the further understanding of the correlation between oxalate and wood degradation;

2) It is necessary to develop the strategies for preventing migration of metal content into wood and removing the metal content off the wood, especially under the preservation environment with uncontrollable humidity conditions.

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