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On the identification of the diffusion ageing mode of Ni/Cu assemblies

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Abstract. This paper focuses on the prediction of one ageing mode of a multilayered material. Ageing is caused by the presence of a chemical gradient that gives rise to diffusion. This work aims at studying the thermo-mechanical and diffusion couplings. Ageing (*i.e.*, diffusion) generates a gradient of thermal and mechanical properties whose coefficients can be obtained by homogenisation techniques. Because of the low scale of observation, practical studies are performed by an EDX method in an SEM. It enables us to measure concentration profiles with a very good accuracy if measurement artefacts, such as the effect of the pear shaped volume of X-ray emission, are accounted for. It follows that the chemical composition of bellows is measured and allows us to evaluate the kinetics of elastic and thermal coefficients of the material with time.

Introduction

The study is concerned with a high precision pressure sensor. It uses bellows that convert a pressure difference into a displacement. The high precision and airtightness of bellows require to make them as a Ni/Cu/Ni (overall thickness: 100 μ m) layered material obtained by an electrodeposition process on an aluminium mandrel that is dissolved in a potassium hydroxide bath to obtain the bellows (see Fig. 1a). Since nickel grows in a nodular shape during the process (Fig. 1b), it cannot provide the required airtightness. Conversely, copper deposits in a continuous multilayer that is able to prevent helium diffusion through the thickness. Consequently, a copper layer is inserted between two layers of nickel. This configuration allows one to minimise the "softening" effect of copper on the mechanical behaviour of bellows since bending is the predominant loading pattern.

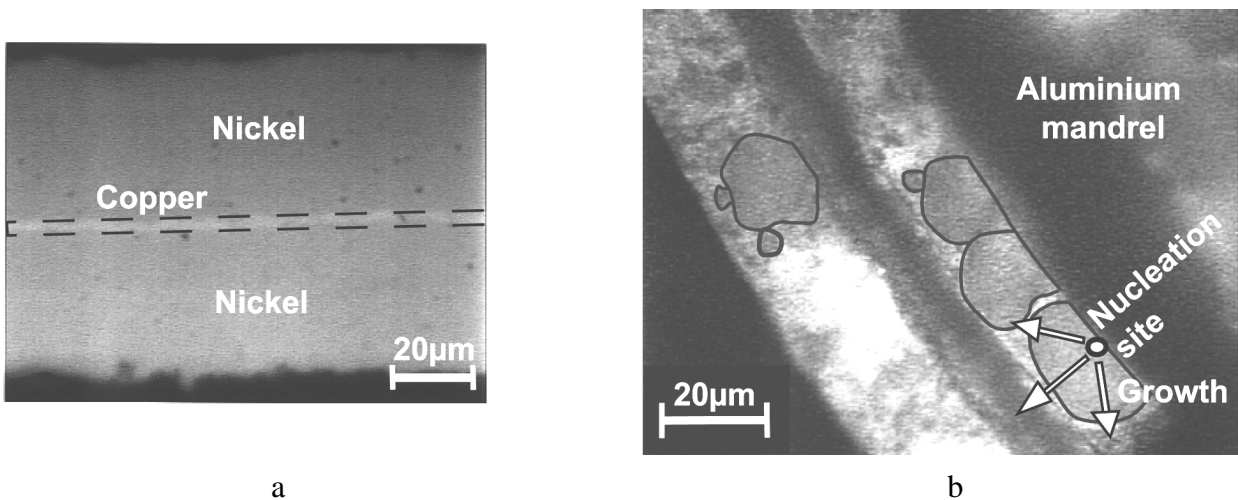


Figure 1. a) Optical micrograph of the multilayered material. b) Optical micrograph in polarised light of nickel nodules after chemical corrosion with regal water.

Such components are expected to stay in-service for many decades, thus they require to predict the material's ageing mode. The study of the main energies (from whom the driving forces are derived) available in this configuration allows one to list the ageing mode that might happen. Numerous ageing modes are possible and must be investigated but the most important one for this configuration seems to be caused by the chemical gradient that gives rise to Ni/Cu diffusion (another mode might be an evolution of the granular structure for example). Consequently, the mechanical behaviour of the bellows will evolve over time and the determination of the diffusion coefficients in this case enables one to predict stiffness changes induced by diffusion. This paper first focuses on a short presentation of the couplings that can be expected between mechanical properties, which are restricted to elasticity, interdiffusion and heat transfer. Then, practical studies of diffusion and the determination of the associated coefficients are performed for moderate temperatures. Finally, homogenisation techniques allow us to evaluate the change of the thermo-mechanical properties of the effective material with time.

Thermo-mechanical and diffusion couplings

The different couplings of interest are presented in Fig. 2.

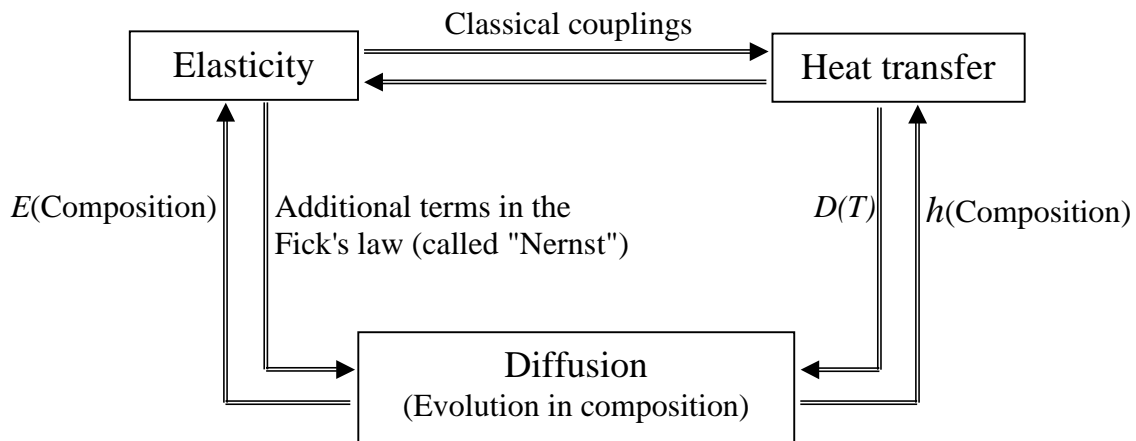


Figure 2. Overall view of the thermo-mechanical and diffusion couplings.

The linear behaviour of materials is now well known, thus the thermo-elastic coupling can be studied with a classical formulation, which is based on the expression of thermodynamic potentials and the derived state laws [1]. The effect of the temperature on diffusion is modelled by an Arrhenius law for the evolution of the diffusion coefficient D with temperature T . The influence of elasticity on diffusion has not been studied yet but has been discussed by Philibert [2] or Beke [3]. Finally, the dependence of the coefficient of thermal conductivity h and the elastic modulus E with the chemical composition of the bilayered material can be obtained by using the same homogenisation techniques. Therefore, the change of these coefficients with time is determined since diffusion coefficients are known.

Practical studies of diffusion

Bellows are usually utilised at an average temperature close to room temperature. For this range of temperature, grain boundary diffusion is predominant over volume diffusion [4]. Usually, it is necessary to analyse separately these two mechanisms. However, for electroplated material, the microstructure is so small (Fig. 1) compared to the scale of observation that the two diffusion modes have not been distinguished. The investigations are limited to the determination of global diffusion coefficients.

Concentration profiles measurement

Increasing the temperature allows one to activate the diffusion process and high rates of diffusion are therefore obtained in reasonable time durations. It is important to note that the relative importance of the two mechanisms of diffusion is modified and that other mechanisms could be activated. The evaluation of diffusion coefficients requires low scales of observation. Therefore, practical studies are performed by an EDX method in an SEM. It enables one to identify and quantify the chemical compounds within a depth of about one micrometer. A mass concentration resolution of about one percent can be obtained in suitable conditions, *i.e.*, measurement artefacts must be considered.

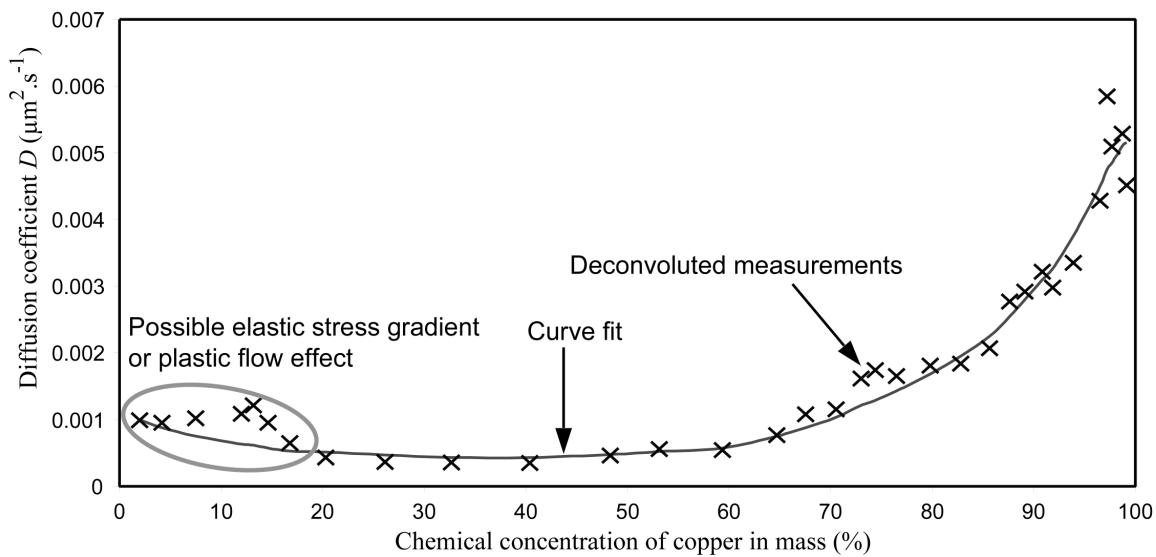


Figure 3. Global diffusion coefficient for 700°C.

The software used to analyse the results of an EDX microprobe usually corrects standard artefacts. However, in the case of diffusion profile, there is an artefact that is generally not treated. It can be called *pear effect* and is caused by the shape of the X-ray emission volume whose dimensions can be of the same order of magnitude as the penetration length of diffusion. A quantitative study of this phenomenon in the case of close atomic number elements (such as nickel and copper), if no dependence of the coefficient of diffusion with the composition is assumed, has shown that the apparent diffusion coefficient D^* measured by an EDX probe follows the simple law [5]

$$D^* = D + \sigma^2/2t, \quad (1)$$

where D is the true diffusion coefficient, σ is a parameter representative of the X-ray emission volume, which is identified on a sample without diffusion, and t the time duration of diffusion [5]. This study is easily extended to composition-dependent diffusion coefficients if the diffusion profile is discretised.

Diffusion coefficient determination and validations

The Boltzmann-Matano method [4] is applied to evaluate the diffusion coefficient (which is dependent on the chemical composition) from the concentration profiles. Special samples (with only one layer of each material) of the diffusion couple are used in which the thickness of each layer is sufficient to prevent the diffusing species to reach a free surface. The true diffusion coefficient is deconvoluted from the raw evaluation with Eqn. (1) and the change with the chemical composition is shown in Fig. 3. One can note, as in Ref. [6], that the diffusion coefficient increases

with the concentration in copper but also for very low concentrations. Since this observation is not detected at lower temperatures of diffusion, we expect that this could be due to an elastic stress gradient effect [7] or a plastic flow induced by a coefficient of thermal expansion mismatch. The dependence of the coefficient with temperature is identified with different testing temperatures. Thus the coefficient of thermal activation of the Arrhenius law is known, with an average value of about 120 kJ.mol^{-1} for temperatures ranging from 500°C to 700°C . Numerical diffusion simulations for any time duration, geometry and temperature (in the same range as in the tests) can be performed. Validations of the previous coefficients have been carried out on the bellows' geometry with a complex temperature cycle. Very good agreement is observed between the simulation and the deconvoluted measurement (Fig. 4 where a diffusion anisotropy is measured and could be due to residual stresses generated during the electro-deposition process. Further studies are needed to explain this observation). Finally, comparisons with literature data confirm our conclusions [8, 9] and the fact that grain boundary diffusion is predominant even for these "high" temperatures.

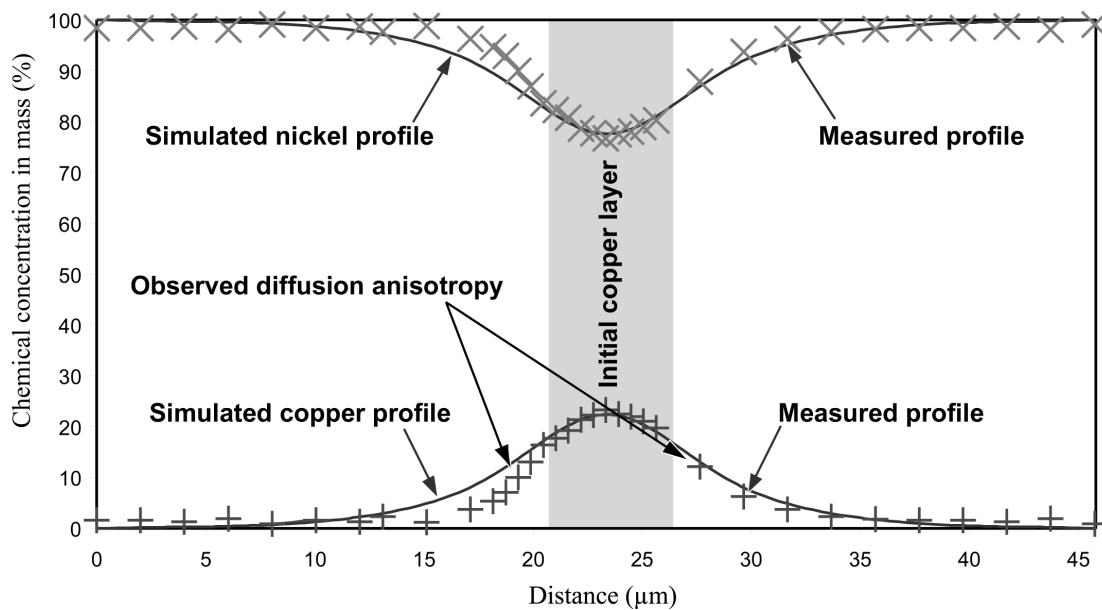


Figure 4. Comparison between simulated concentration profiles and the associated deconvoluted measurements.

However, as expected, these coefficients (and especially the dependence of the linear extrapolation of the thermal activation coefficient to lower temperatures) are not able to simulate the observed diffusion on bellows aged at room temperature during many years. However, we can assume, as a first approximation, that concentration profiles are not modified by the temperature but only by the time duration. This allows us to determine the evolution of the elastic coefficients with time and to draw conclusions on long-term reliability of bellows.

Homogenisation of the elastic modulus: change with time

The change of the effective elastic properties (*i.e.*, transverse, longitudinal and in-plane shear moduli) of the bilayered material with the diffusion process is evaluated. Since the Poisson's ratios of the two materials are very close, we assume that the effective one is not influenced by diffusion. The determination of the effective coefficients, when the chemical composition is known, is illustrated in Fig. 5. The diffusion curves are discretised to obtain a multilayered material in which each layer is assumed to have a constant chemical composition and to be isotropic. The effective elastic modulus is obtained by using a homogenisation scheme consistent with the principal diffusion mode: grain boundary diffusion. Therefore, in the nickel layer, we find grains of the latter surrounded by copper and the opposite situation in the copper layer (Fig. 6). The generalised self-consistent scheme [10] is the most suitable one and the two corresponding bounds are necessary

(for the thermal conductivity see Ref. [11]). When this first step is completed, we have a composite-like material with isotropic elastic layers and a homogenisation scheme applied to multilayered materials is used to evaluate the overall anisotropic elastic properties.

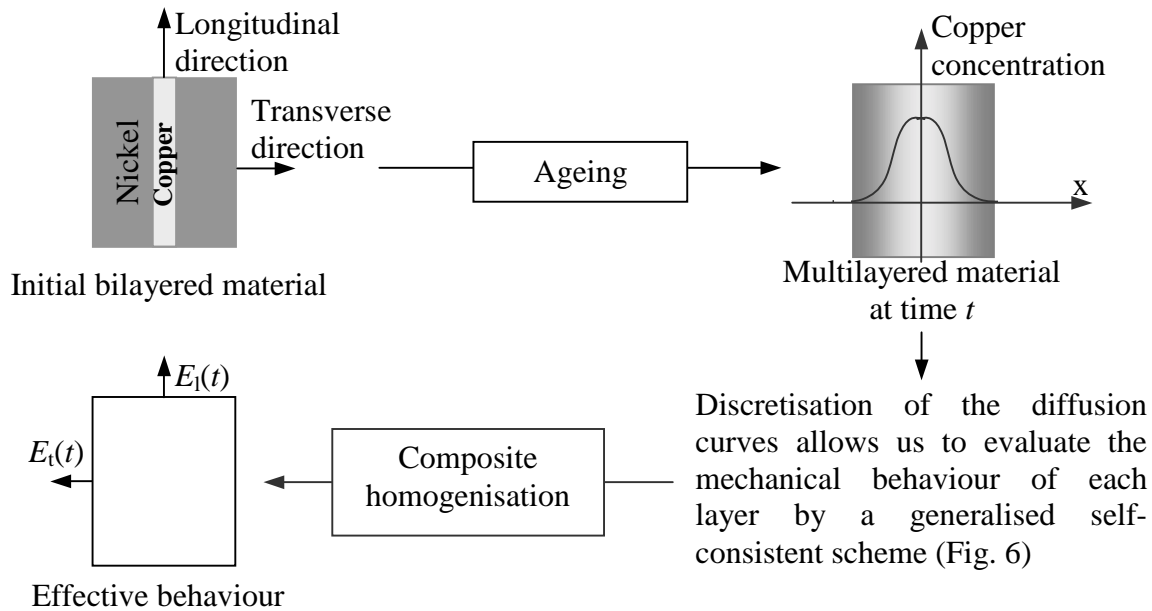


Figure 5. Homogenisation steps to predict the overall elastic properties.

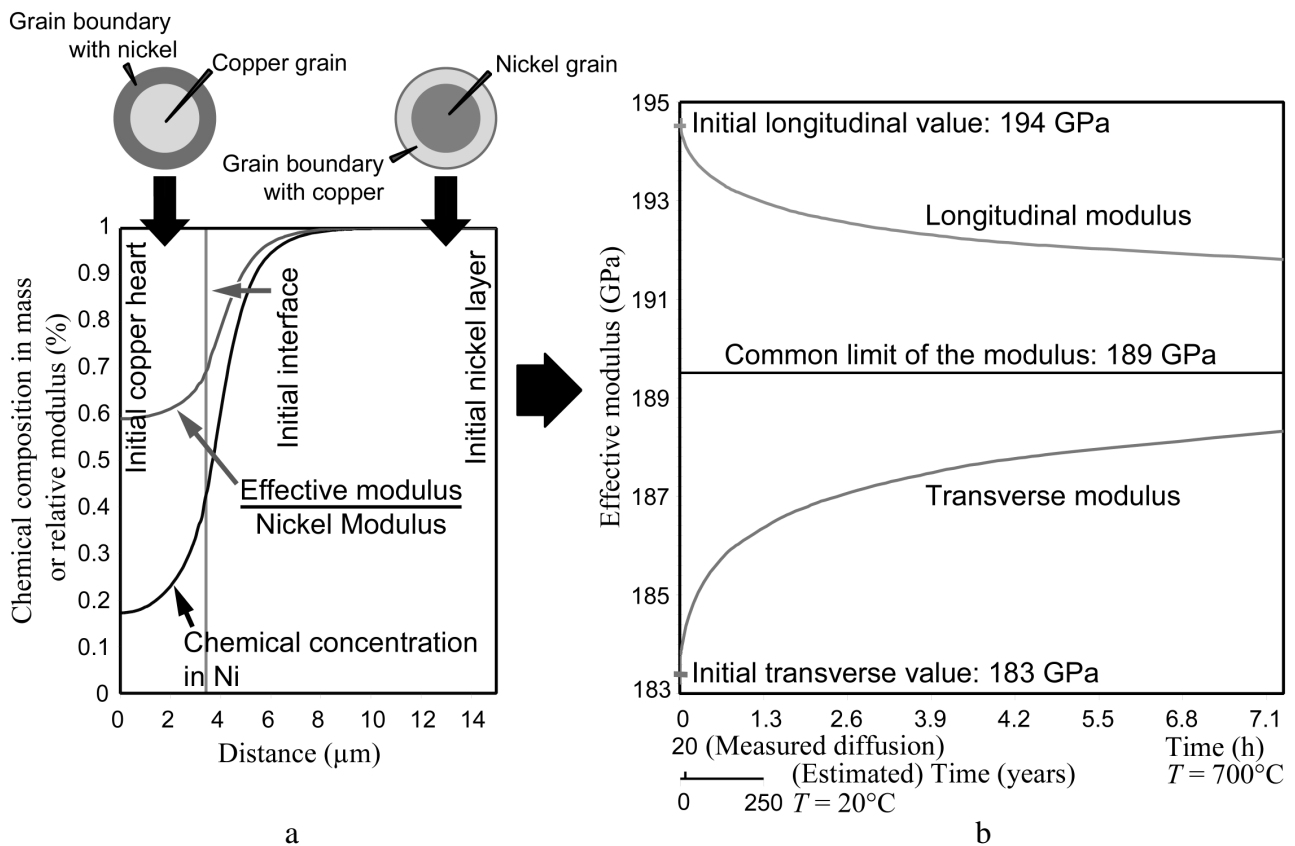


Figure 6. a) First homogenisation step (37 minutes, 700°C) on one half of the bilayered material. b) Second homogenisation step: effective elastic modulus vs. time for $T=700^{\circ}\text{C}$ and an estimation of the equivalent time for $T=20^{\circ}\text{C}$ based on a measured diffusion profile.

Discussion and conclusions

Simulations of diffusion at any time are possible with the determined coefficients and allow us to have the corresponding elements' concentration profile. Thus, effective elastic moduli are obtained at each time with the homogenisation techniques presented above. An illustration of the first "step" is shown in Fig. 6a. The transverse and longitudinal moduli are deduced from the second homogenisation step (Fig. 6b). It is worth noting that the magnitude of variation of the modulus depends on the relative thickness of the copper and nickel layers. We point out that the maximum magnitude of variation is obtained in relative short time duration, *i.e.*, ageing mode by diffusion could be significant even for low time durations or temperatures. For example, a rough approximation based on an equivalence on the average rate of diffusion for a 20 year ageing material gives an idea of the corresponding time duration at room temperature (Fig. 6b). However, the relative effect of the two diffusion mechanisms evolves with temperature and more investigations have to be performed. Since the stiffness of bellows is proportional to the longitudinal modulus (for relatively low deflection), the diffusion could have a non-negligible effect on the overall behaviour of the component if the copper layer is too thick. Moreover, diffusion could have an effect on the airtightness of bellows as it degrades the copper barrier and, if the Frenkel effect is confirmed, porosity could appear in copper and lead to crack nucleation. However, a competitive phenomenon occurs in nickel layers where the Kirkendall effect tends to put them in compression. Thus, the initial *porosity* could decrease enough to ensure the airtightness of bellows.

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