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Solartechnik
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Institut für Solartechnik SPF
Hochschule für Technik HSR
Oberseestr. 10, CH- 8640 Rapperswil
Tel. +41 55 222 48 21, Fax +41 55 222 48 44

REPORT

SPF-ITR • Oberseestr.10 • CH-8640 Rapperswil

Bundesamt f. Energie
BFE

3003 Bern

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Stefan Brunold, stb	22.06.2004	-	1 (11)

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Vacuum test for solar absorbers:
Results of three different coatings

Introduction

Accelerated examinations concerning the ageing are meanwhile an established method to examine the long-term stability of the solar absorber coatings. This well described test, however, is limited to absorber coatings for the use in covered flat plate collectors.

The present report presents the results of tests concerning the stability of solar absorber coatings for the use in not concentrated, evacuated collectors. The tests are based on the same principles as those already in use for the above mentioned methods.

Due to limited resources not all absorber coatings that are currently available in the market can be included into the test. As an example, the presented results are therefore limited to three absorber coatings deposited with a different coating technology.

1. Basics

The accelerated ageing tests that have been performed are based on the assumption that the operation speed of the processes that lead to degradation are temperature-dependant. This dependence can be described by the Arrhenius' relation. This means in particular that the increase of temperature accelerates the degradation. Thus, the actual thermal stress which a solar absorber is exposed to in a solar collector for 25 years, can be simulated in the laboratory over a significantly shorter period of time (however with higher temperature).

On the one hand, the assumed Arrhenius' relation can be confirmed by the determination of the time dependence of the degradation progress for different temperature levels; taking the activation energy E_A as a parameter. However, on the other hand, predictions about the resistance of the absorber in a real solar collector can be made by elementary transformations. The physical and mathematical details of this procedure are described in several publications [1 – 7].

In order to keep the necessary transformations as simple as possible, it is advantageous to conduct the laboratory tests at a constant temperature. In particular, this implies that the times to heat up and cool down are to be kept as short as possible. This leads to the claim to reduce the thermal masses which have to undergo a temperature change to a minimum.

Therefore a special vacuum oven has been constructed (see figure 1.1) which meets these requirements. This oven consists of a hot zone of constant temperature and an actively cooled zone. After the hot zone has reached the examination temperature, the samples are relocated into this area with a sample trolley. When the testing time has elapsed, they are rolled back into the cooled area. So it is not necessary to change the temperature of masses, except for the samples and the sample trolley.

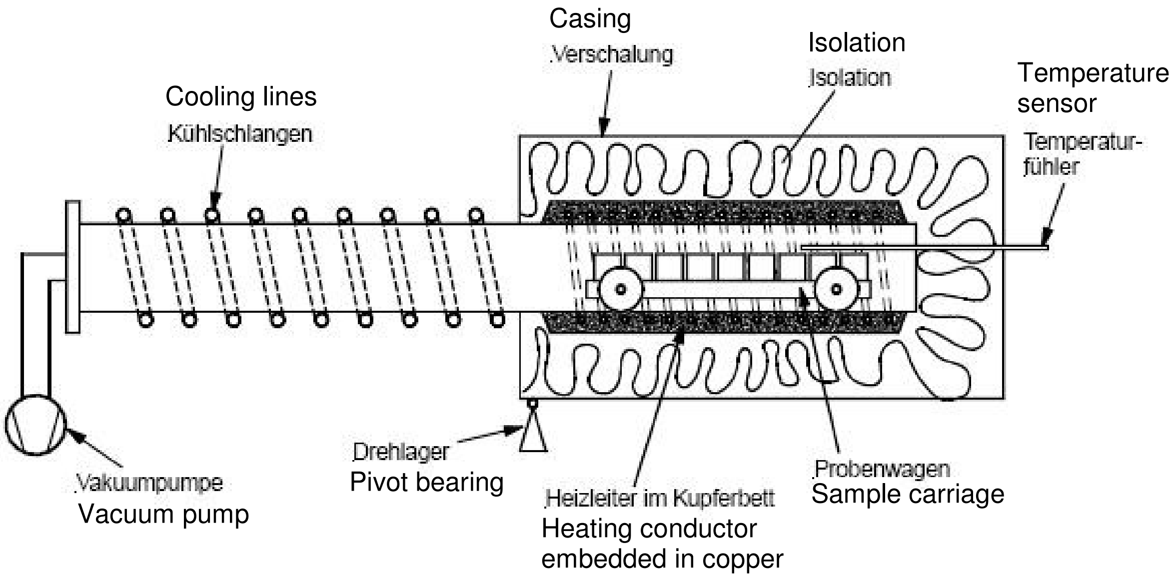


Figure 1.1: Vacuum oven with sample trolley in the heated area. By tilting, the trolley can be moved to the heated (cooled) area on the right (left) for faster heating up (cooling down).

For the determination of the thermal stress exposed to an absorber in a vacuum tube of a solar thermal collector, the effective medium temperature T_{eff} is used. This temperature can be determined by the Arrhenius transformation by the integration of the factual progress of the absorber temperature. Therefore, it is a function of the activation energy E_A. Generally, the integration period is one year. So the strain on an absorber in a solar collector during one year is the same as the strain at a constant temperature T_{eff}, also for the period of one year.

As the development of the absorber temperature over the time is primarily dependant on the design of the solar system, yearly simulations have been calculated by Polysun [9] for the following five different types of solar systems:

1. hot water for domestic use in a one-family house
2. hot water for domestic use with heating support in a one-family house
3. hot water for domestic use in an apartment building
4. big refrigerating plant with a high solar fraction
5. industrial process heat installation

For each type of installation, a 20-day period of stagnation in summer was assumed as an aggravation of the normal operation.

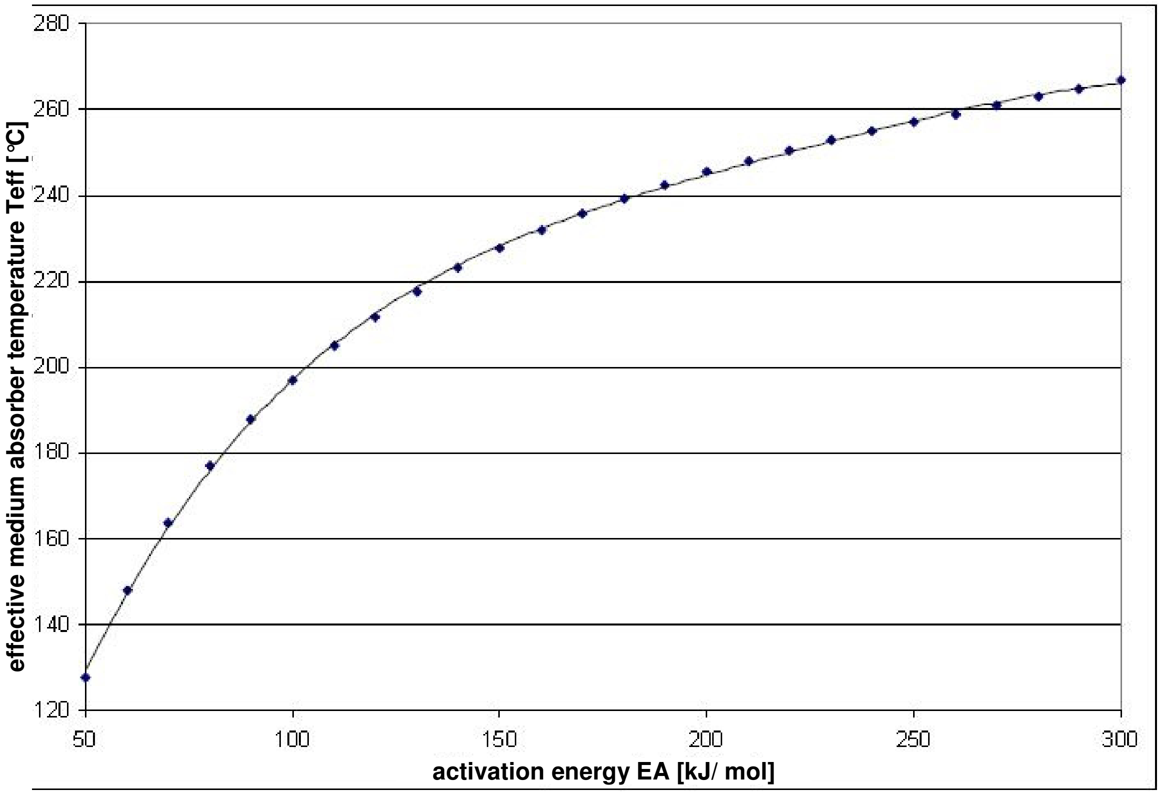


Figure 1.2: Effective medium absorber temperature for vacuum tubes with 20 (summer) days stagnation per year (no concentrating systems).

Subsequently, the effective medium temperature T_{eff} (see figure 1.2) has been calculated from the simulated temperature development. This leads to the conclusion that the thermal stress of the absorber is practically dominated by the stagnation time. Only to a small extent the effective medium temperature is dependant on the type of installation. Therefore, it is not necessary to distinguish between the five types of installation mentioned above. However, it has to be observed that this outcome must not, in any case, be expanded totally to other systems (e. g. parabolic trough powerplants etc.), without making the necessary calculations.

In order to quantify the modification of the performance of an absorber coating, Hollands et al. has conducted extensive parameter studies by means of a computer simulation. The "performance criterion" (PC) has turned out to be a useful value, which describes the influence of the change in the solar absorbance $\Delta\alpha_s$ and the thermal emissivitiy Δ_ε on the solar fraction:

$PC = -\Delta\alpha_s + k * \Delta_\varepsilon$ (equation 1.1)

The value of the "performance criterion" of 0.05 corresponds to a loss of the yearly solar fraction of an installation for a domestic hot water of 5 %. If this loss is considered to be acceptable as the maximum tolerance, the time that elapses until this value will be reached is called "failure time".

The parameter k (in equation 1.1.) is a dimension for the influence of the emissivity on the capability of a solar collector - in comparison to the absorbance. For domestic hot water installations with standard flat plate collectors the parameter k equals 0.25 (k = 0.25). For installations with high solar fractions (about 50 % and more) and heating support k equals 0.5 (k = 0.5). This value is used in our calculations.

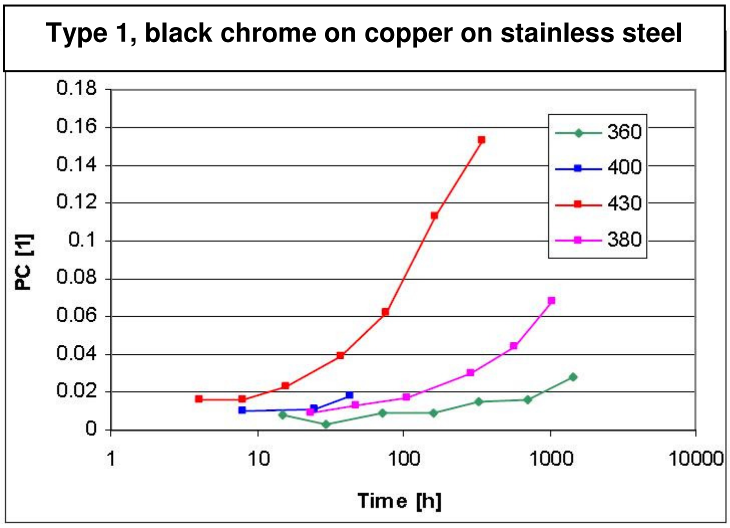
2. Experimental results

2.1 Results for Type 1

Type 1 is a galvanically deposited black chrome layer on a stainless steel substrate with copper as interlayer to minimize the emissivity.

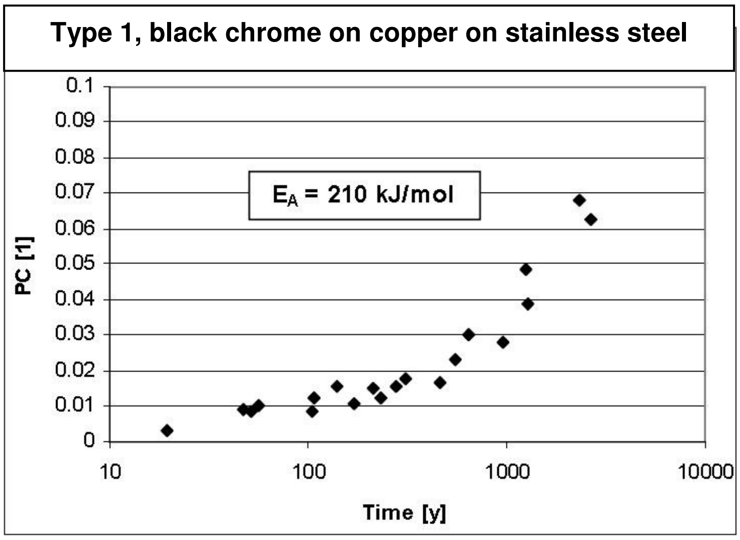
The samples have been tested under vacuum at 360 C, 380 C and 430 C. The changes of the optical properties over the time have been registred (measured) with the spectrometer. With this data, the degree of degradation (PC) has been determined (see figure 2.1.1).

Figure 2.1.1:
Change of the optical properties of the layer over time at different temperatures under vacuum conditions.



These four different degradation lines could be converted to a progression line at an effective medium temperature t_{eff} = 247 °C (figure 2.1.2) by conducting an Arrhenius transformation with an action energy of E_A = 210 kJ/ mol. According to this evidence, the failure of the coating could be anticipated after a period of more than 1,000 years (PC > 0.05). In the relevant period of 25 years, a loss of performance of approximately 1 % needs to be expected.

Figure 2.1.2: Progression of the degradition of an effective medium temperature of 247 °C. The durability of the coating (PC > 0.05) exceeds the requested minimum durability of 25 years considerably.



For the analysis of the coating Auger spectroscopy (AES) has been used. Depth profiles have been prepared, taking both an untouched sample (figure 2.1.3) and a sample after a stress of 1368 hours at 360 °C (vacuum) has been prepared (figure 2.1.4). The PC of the sample under stress is 0.028 at the time of the analysis. For this sample, the requested minimum durability of 25 years has been exceeded by far.

Type 1, black chrome on copper on stainless steel

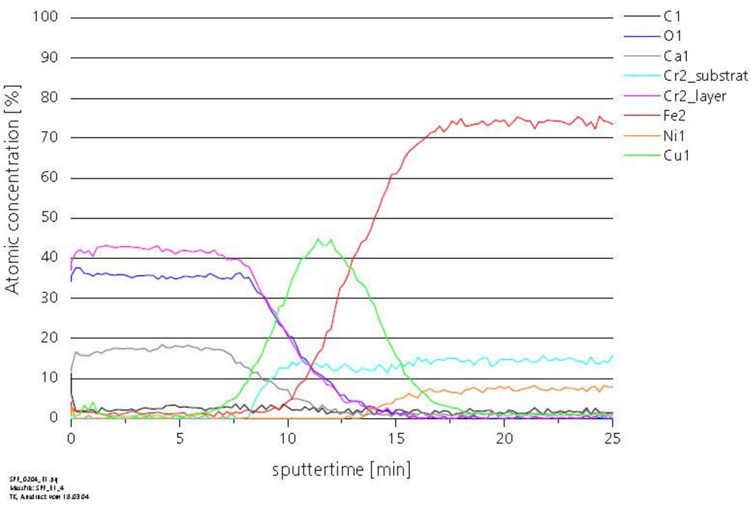


Figure 2.1.3: Auger Depth Profile of an untouched sample.

The *"sputtertime"* (x-coordinate) is a dimension for the depth. A *"sputtertime"* of 0 min corresponds to the surface of the coating.

Type 1, black chrome on copper on stainless steel

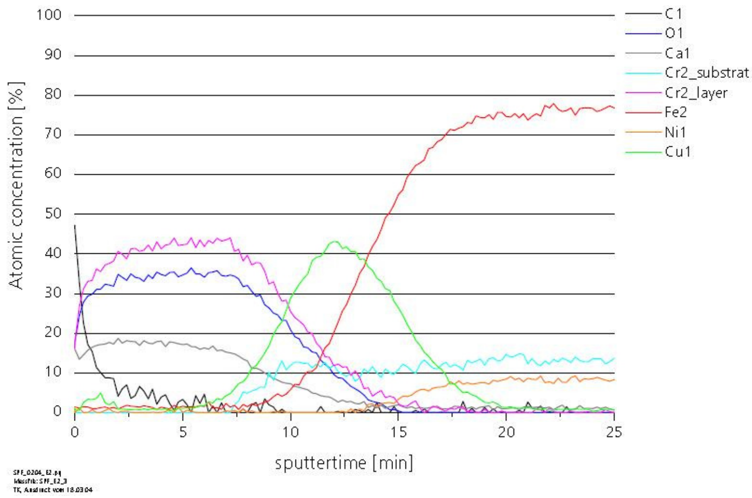


Figure 2.1.4: Auger Depth Profile of a sample after 1468 hours at 360 °C (vacuum)

The comparison of both profiles shows that the intermediate layer (= copper) will spread out slightly into the substrate by the thermal stress due to diffusion. Even less copper is to be found on the surface of the coating. Both effects lead to a slight decrease of both the absorption and the emissivity. This has been observed with optical measurements. However, the degradation of the absorbance exceeds the emissivity. Therefore, the capability decreases and the PC increases.

The apparent decrease of chrome and oxygen on the surface of the coating of the sample under thermal strain is to be attributed to the ocurrence of carbon. It is supposed that this is due to impurities which have got onto the surface after the trials.

Conclusion:
The performed tests lead to the conclusion that the absorber coating of type 1 is suitable for application in vacuum collectors for the following 5 types of applications:

1. hot water for domestic use in a one-family house
2. hot water for domestic use with heating support in a one-family house
3. hot water for domestic use in an apartment building
4. big refrigerating plant with a high solar fraction
5. industrial process heat installation

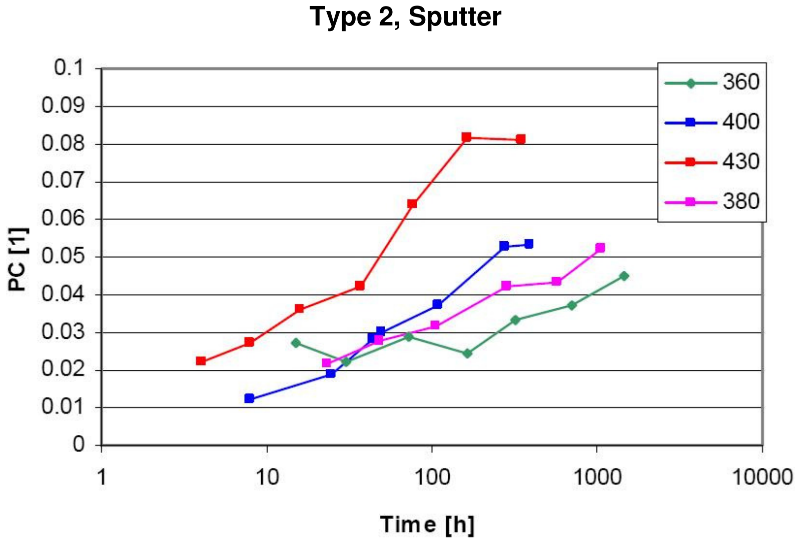
It is not possible to give any statement regarding concentrating systems as these have not been part of the studies!

2.2 Results for Type 2

Type 2 is a chrome-oxide coating deposited by sputtering on a copper substrate with a final coating of tin oxide for antireflection.

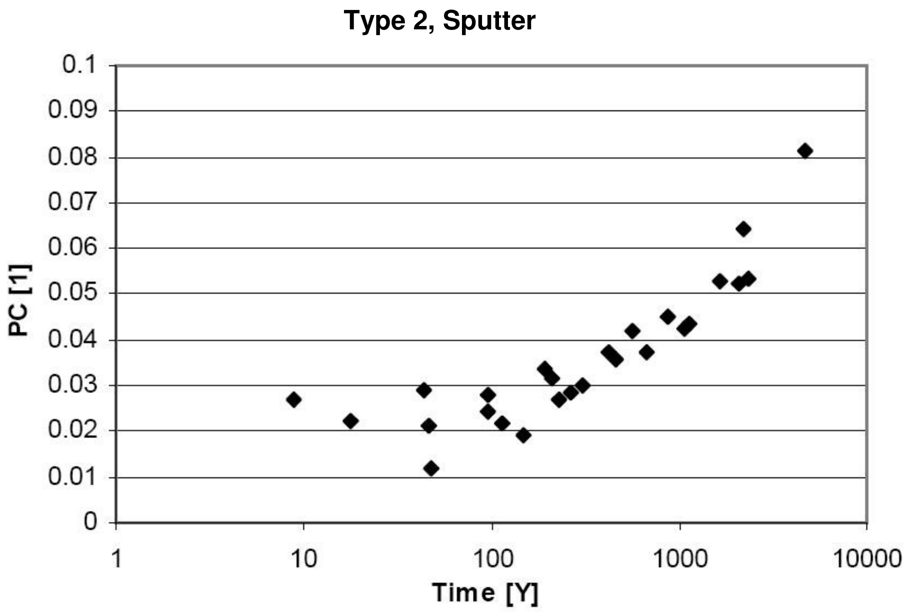
The samples have been tested under vacuum at 360 °C, 380 °C, 400 °C and 430 °C. The change of the optical properties over time has been measured with a spectrometer. With this data, the extent of the degradation (PC) has been determined (see figure 2.1.1).

Figure 2.1.1: Change of the optical properties of the coating over time at different temperatures under vacuum.



These four different degradation lines could be converted to a progression line at an effective medium temperature t_{eff} = 247 ℃ (figure 2.1.2) by conducting an Arrhenius transformation with an action energy of E_A = 210 kJ/ mol. According to this evidence, the failure of the coating could only be anticipated after a period of more than 1,000 years (PC > 0.05).

Figure 2.1.2: Progression of the degradition of an effective medium temperature of 247 ℃. The durability of the coating (PC 0.05) exceeds the requested minimum durability of 25 years considerably.



For the analysis of the coating, the Auger spectroscopy (AES) has been applied. Depth profiles have been prepared, taking both an untouched sample (figure 2.1.3) and a sample after a stress of 1368 hours at 360 ℃ (vacuum) has been prepared (figure 2.1.4). The PC of the sample under stress is 0.045 at the time of the analysis. For this sample, the requested minimum durability of 25 years has been exceeded by far.

The ‚*sputtertime*' (x-coordinate) is a measurement for the depth. A '*sputterime'* of 0 min corresponds to the surface of the layer.

Type 2, Sputter

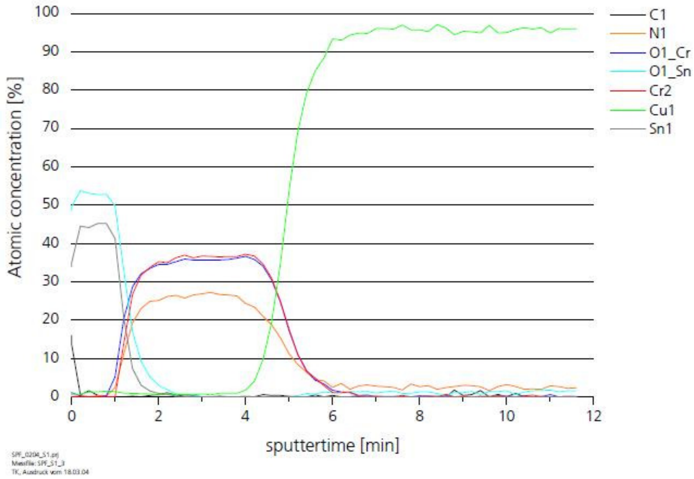


Figure 2.1.3: Auger depth profile of an untouched sample.

Type 2, Sputter

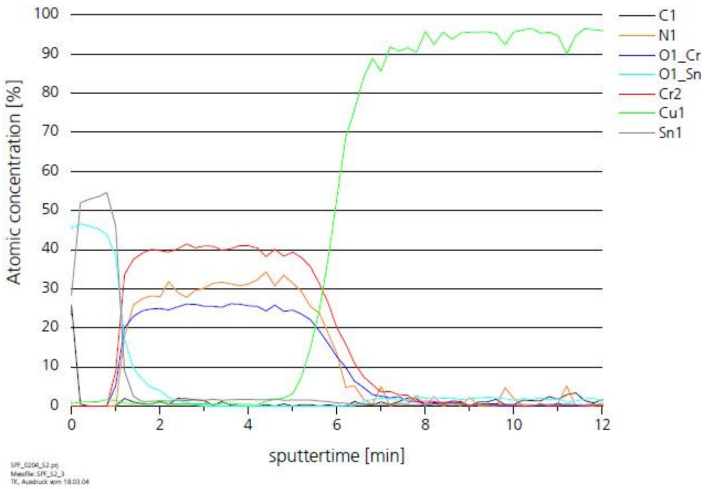


Figure 2.1.4: Auger depth profile of a sample after 1368 hours at 360 °C (vacuum).

The comparison of both profiles shows that the oxygen content of the coating is decreasing considerably by the thermal stress under reduced atmosphere (vacuum). So the relative concentration of tin rises in this coating resulting in a more “metallic” coating and a higher index of refraction. Thus, this coating alloys its characteristics as an antireflection coating and the absorption capacity decreases.

The loss of oxygen extends itself up to the functional coating (between 1 and 5 minutes sputtertime), making the coating also more “metallic”. This involves a further decrease of the absorption, but also to a decrease of the emissivity. This effect could also be observed by optical spectroscopy. However, the degradation of the absorption outbalances the emissivity. In total, the performance decreases whereas the PC increases.
It is worth noting that the sample under thermal stress taken from figure 2.1.4 has exceeded the minimum durability of 25 years by far. However, the optical properties of this sample are still satisfactory.

Conclusion:

The performed tests lead to the conclusion that the absorber coating of type 2 is suitable for application in vacuum collectors for the following 5 types of applications:

1. hot water for domestic use in a one-family house
2. hot water for domestic use with heating support in a one-family house
3. hot water for domestic use in an apartment building
4. big refrigerating plant with a high solar fraction
5. industrial process heat installation

It is not possible to give any statement regarding concentrating systems as these have not been part of the studies!

2.3 Results for Type 3

Type 3 shows the titanium oxide nitride coating deposited by reactive evaporation on copper substrate with a cover coating of silicium oxide for antireflection.

The samples have been tested in a vaccum at 360 °C, 380 °C and 430 °C. The changes of the optical properties have been recorded with a spectrometer from time to time. Thus, the extent of the degradation (PC) is determined (see chart 2.3.1).

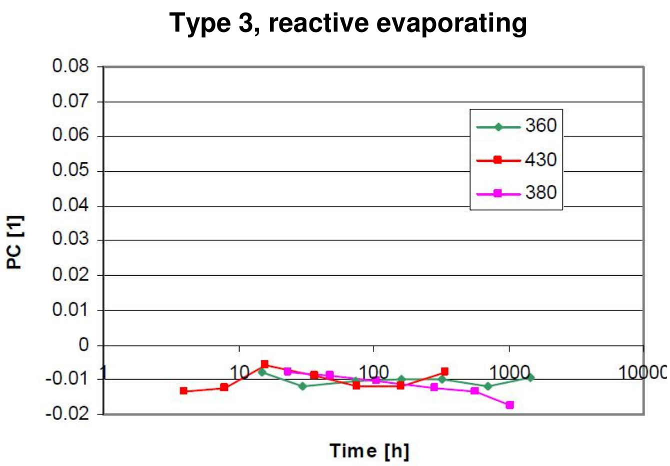


Figure 2.3.1: Change of the optical properties of the coating over the time at different temperatures under vacuum conditions.

As the optical properties of the samples do not change significantly in none of the performed tests, it is not possible to determine any activation energy by Arrhenius Transformation. However, the performed tests lead to a life-time of over 25 years for all activation energies that can be reasonably assumed.

Due to the fact that the optical properties of the coating do not change by thermal stress, an analysis of the coating has been left out.

Conclusion:
The performed tests lead to the conclusion that the absorber coating of type 3 is suitable for application in vacuum collectors for the following 5 types of applications:

1. hot water for domestic use in a one-family house
2. hot water for domestic use with heating support in a one-family house
3. hot water for domestic use in an apartment building
4. big refrigerating plant with a high solar fraction
5. industrial process heat installation

It is not possible to give any statement regarding concentrating systems as these have not been part of the studies!

3. References

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