Development and characterization of Sn99Ag0.3Cu0.7-(ZrO_2/CuO/TiO_2) nano-composite solder alloys

Balázs Illés

Budapest University of Technology and Economics, Department of Electronics Technology (BME-ETT)

Łukasiewicz Research Network - Institute of Microelectronics and Photonics, LTCC Technology Research Group,

Kraków, Poland

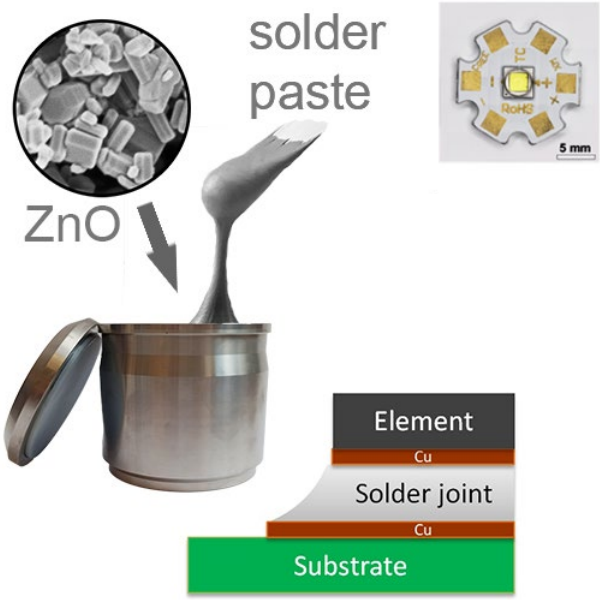
Illes.balazs@vik.bme.hu

Outline/Agenda

- Introduction composite soldering
- Materials and methods
- Results of quality investigations
- Results of reliability investigations
- Discussion
- Conclusions
- Q & A

Composite soldering

- ***Composite solder paste:*** adding reinforcement particles into the solder paste like ZnO, TiO_2, ZrO_2, Al_2O_3, Fe_2O_3, Si_3Ni_4, SiC, La_2O_3, in 0.05-2 wt%.
- Particles are usually nano-sized.
- Most of the researches investigated bulk the solder alloy and not solder joints.



- Aim: investigate the ***quality and reliability of SAC0307-(ZrO_2/CuO/TiO_2)*** composite solder joints.

Materials and methods

Solder paste:

- Sn99Ag0.3Cu0.7 (SAC0307)

Nano-particles (NPs) in 0.25wt%:

- ZrO_2, primary particle size <100nm
- CuO, primary particle size <50nm
- TiO_2, primary particle size ~21nm

NPs were mixed into the solder paste by a solder paste mixer (15mins and 400rpm)

Materials and methods

Investigated solder alloys:

Name	Composition
SAC0307	Sn99Ag0.3Cu0.7
SAC0307-TiO_2	Sn99Ag0.3Cu0.7-0.25TiO_2
SAC0307-ZrO_2	Sn99Ag0.3Cu0.7-0.25ZrO_2
SAC0307-CuO	Sn99Ag0.3Cu0.7-0.25CuO

Materials and methods

Wetting test:

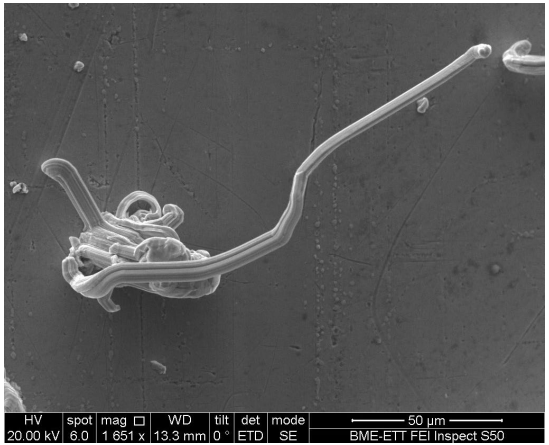
- Standard spread test (IPC-650)

Mechanical test:

- Shear strenght measurements (IPC-650),
- on 0603 SMD chip resistors soldered on PCB.

Reliability test:

- TH test 85ºC/85RH% for 3000h: corrosion resistance and ***Sn whisker growth***



Materials and methods

Wetting test:

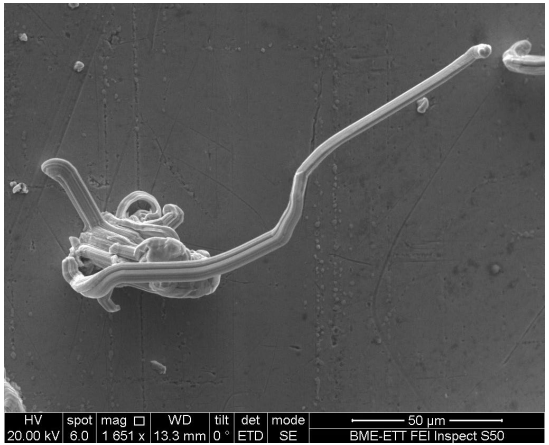
- Standard spread test (IPC-650)

Mechanical test:

- Shear strenght measurements (IPC-650)
- on 0603 SMD chip resistors soldered on PCB.

Reliability test:

- TH test 85ºC/85RH% for 3000h: corrosion resistance and ***Sn whisker growth***

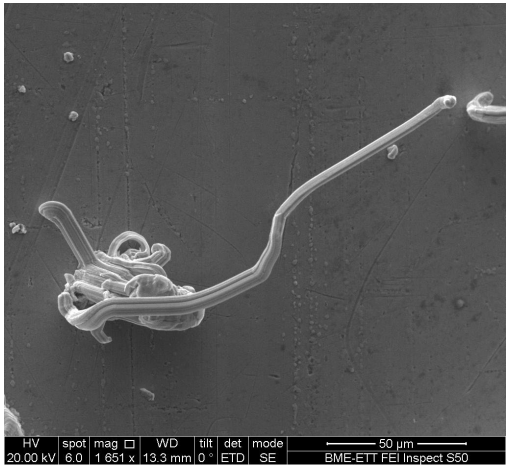


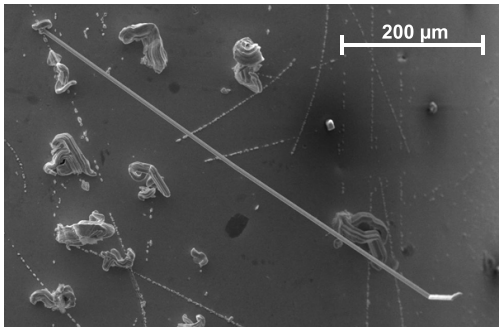
Materials and methods – Sn whiskers

- Sn whiskers are a reliability issue
- Conductive whiskers „spontaneously” grow from Sn surfaces

Mechanical stresses cause whiskering:

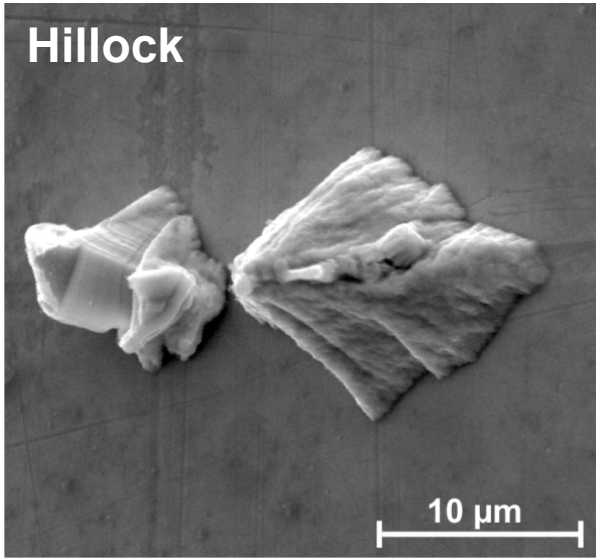
- residual stress in the Sn layer,
- direct external mechanical load,
- volumetric expansion (by intermetallic or ***oxide growth***),
- thermomechanical effects.

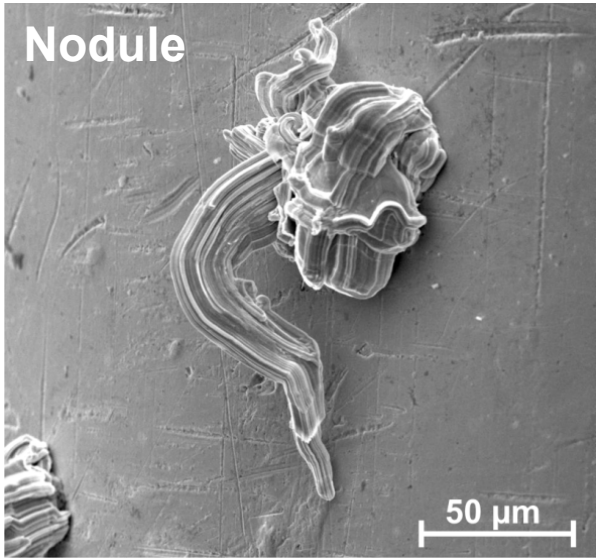


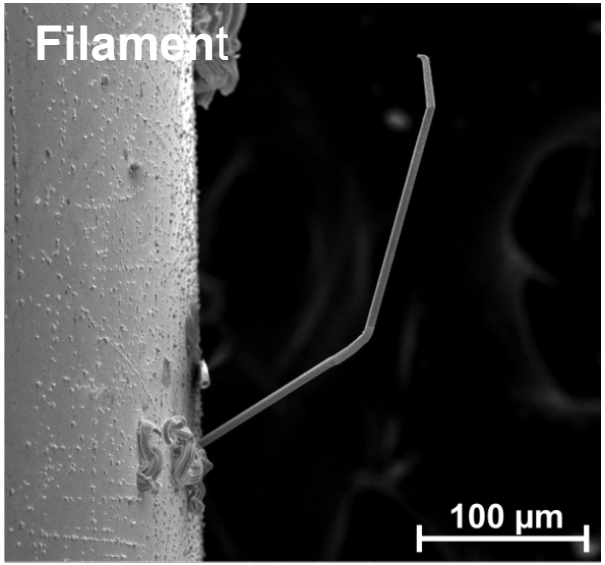


Materials and methods – Sn whiskers

Whisker types: hillock, nodule, and filament



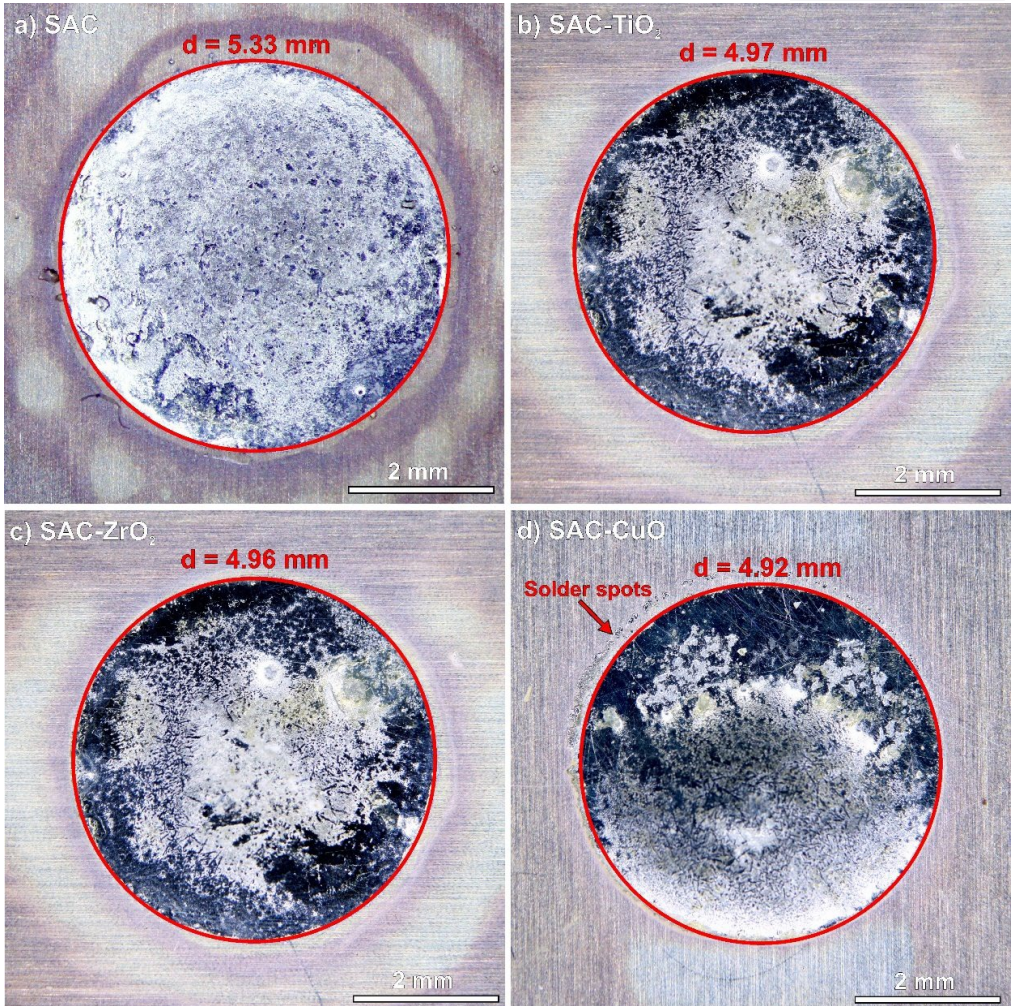




Quality results

Wetting test:

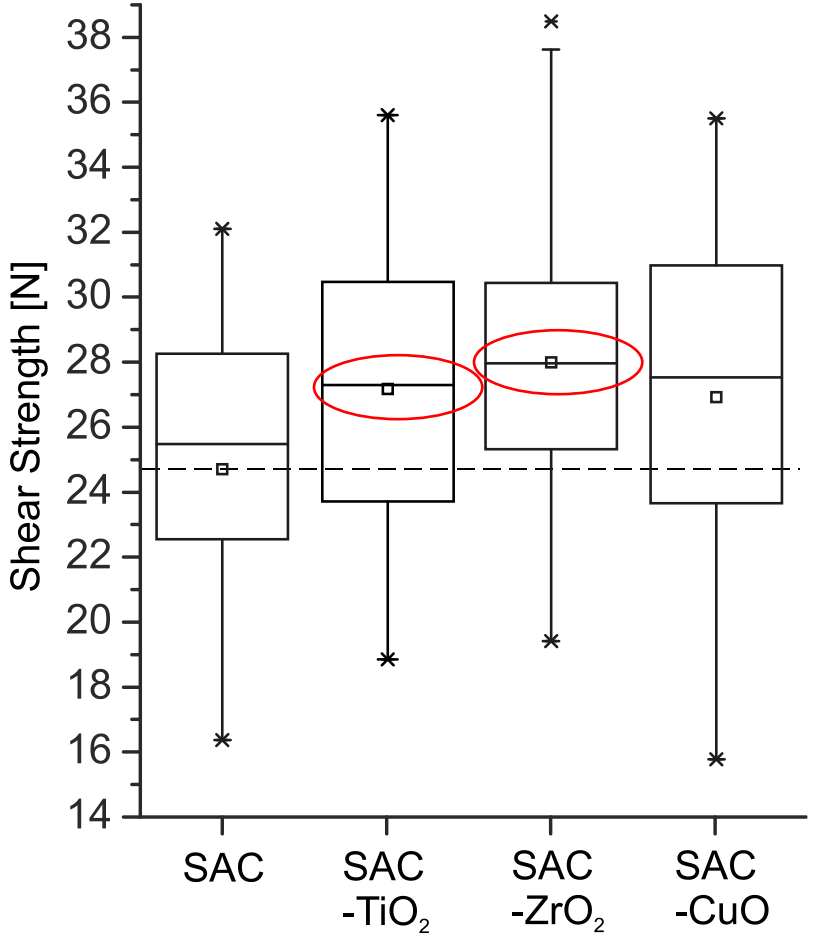
- ***Minor decrease (1-2%) of wetting in the case of nano-composite solder alloys.***
- No major differences between the different NPs.
- CuO showed a bit weaker results than TiO_2 and ZrO_2.



Quality results

Mechanical test (as-reflowed):

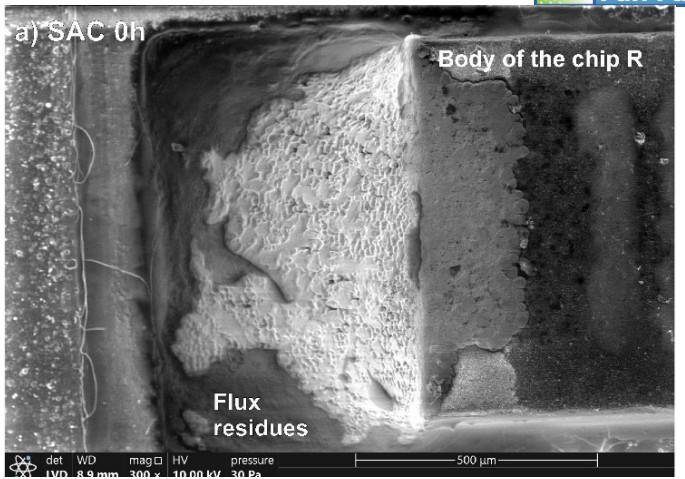
- ***TiO_2, ZrO_2, and CuO NPs increased the shear strength with 10%, 13%, 9%.***
- TiO_2 and ZrO_2 NPs made the shear strength distributions more symmetric.
- CuO showed a bit weaker results than TiO_2 and ZrO_2.

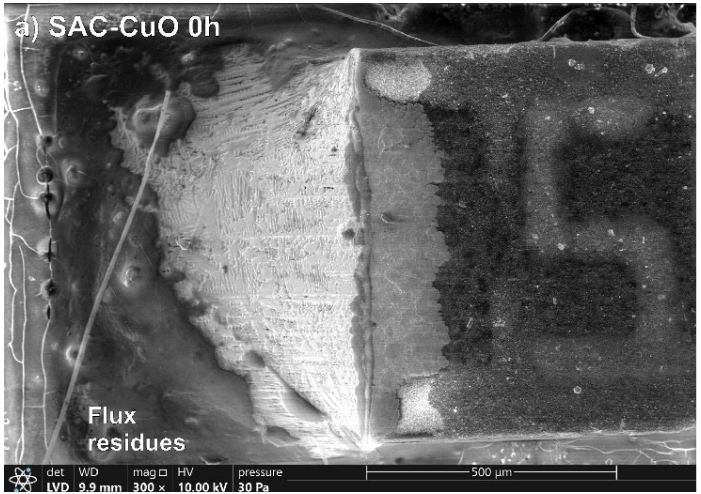


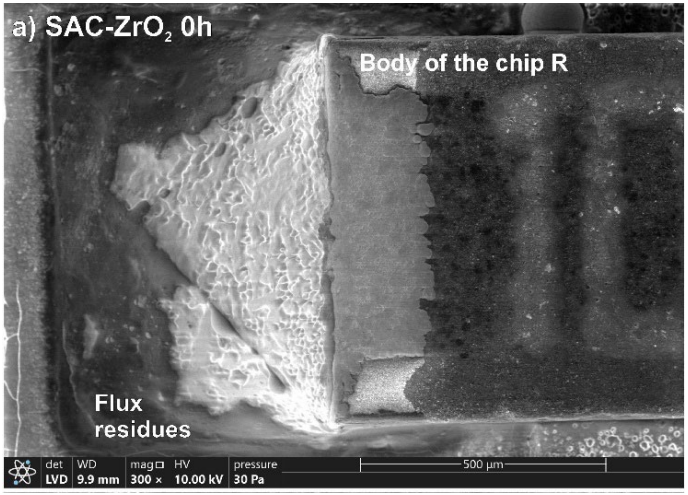
Reliability results

As-reflowed:

- Flux residues at the lower part of the joints, which were removed with IPA.



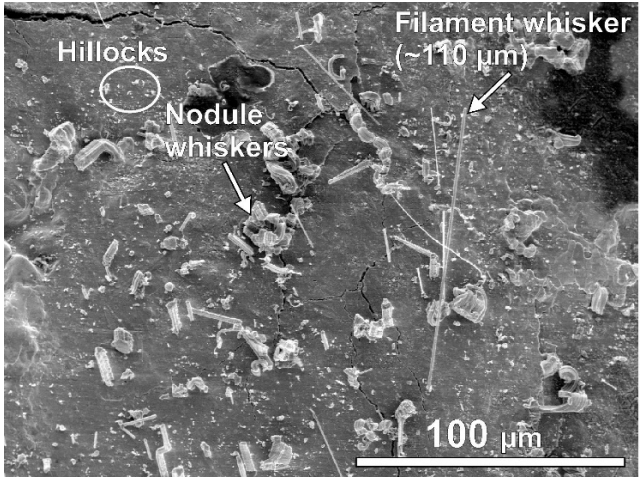


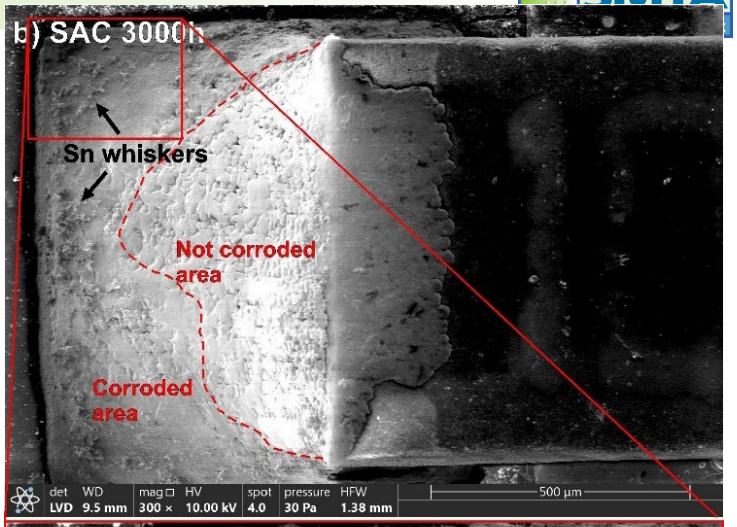


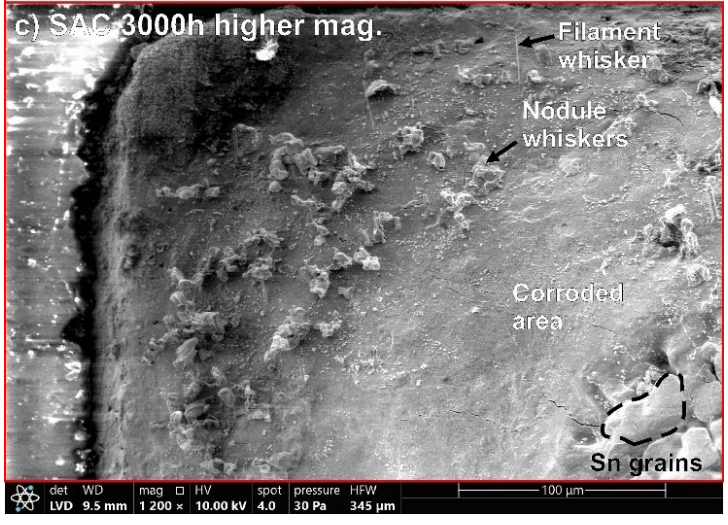
Reliability results

SAC0307 reference after 3000h:

- Reference solder joints suffered ***considerable corrosion***, mainly at the lower meniscus.
- Corroded area contained ***Sn whiskers.***



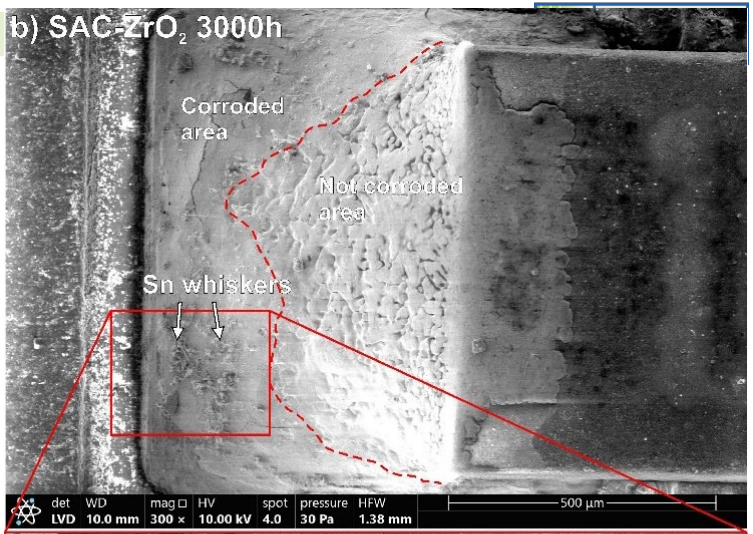


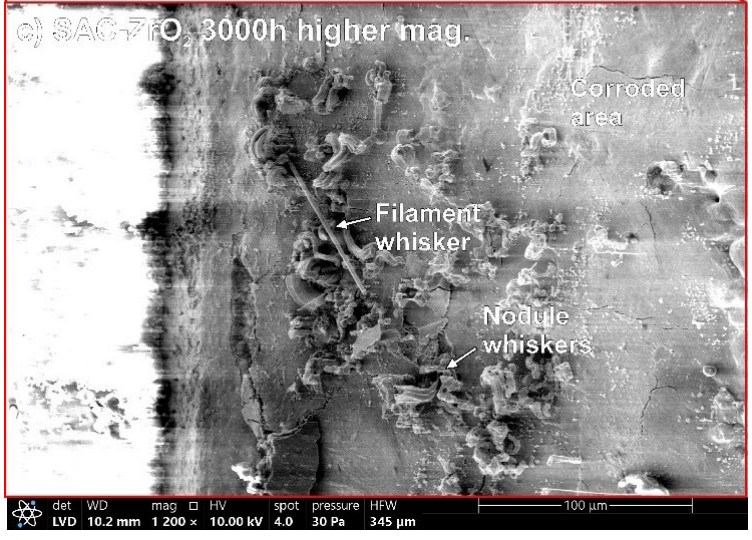


Reliability results

SAC0307-ZrO_2 after 3000h:

- SAC-ZrO_2 joints also corroded at the lower part of the meniscus.
- ***ZrO_2 NPs did not modify the corrosion resistance***.
- Sn whiskers grew from the corroded areas, but may be in lower amount than on the reference joints (detailed statistical evaluation later)

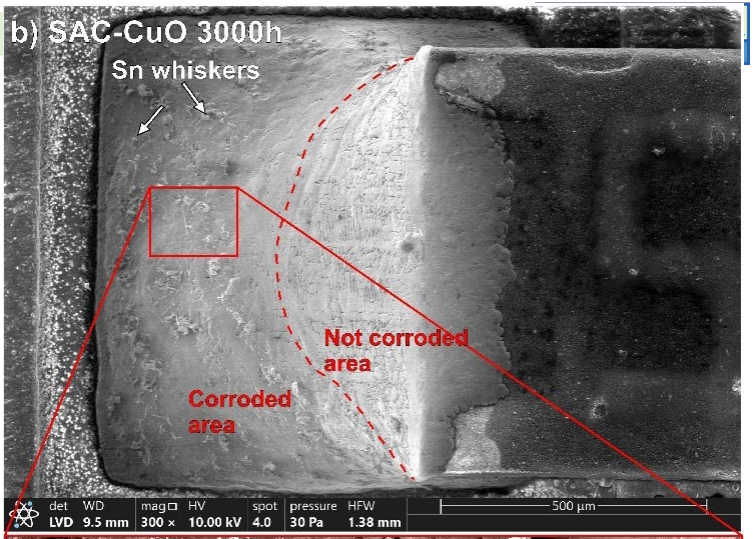


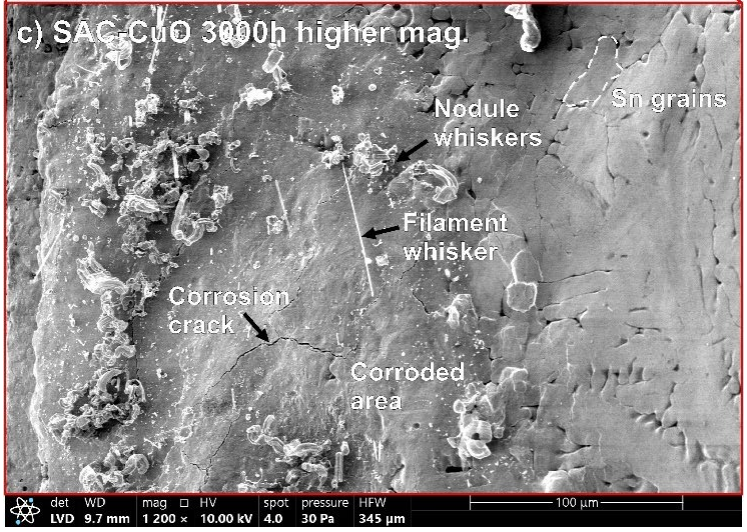


Reliability results

SAC0307-CuO after 3000h:

- SAC-CuO solder joints suffered the most serious corrosion.
- ***CuO NPs decreased the corrosion resistance*** of the nano-composite solder joints.
- Number of Sn whiskers was higher than in the case of the reference and SAC-ZrO_2 samples.

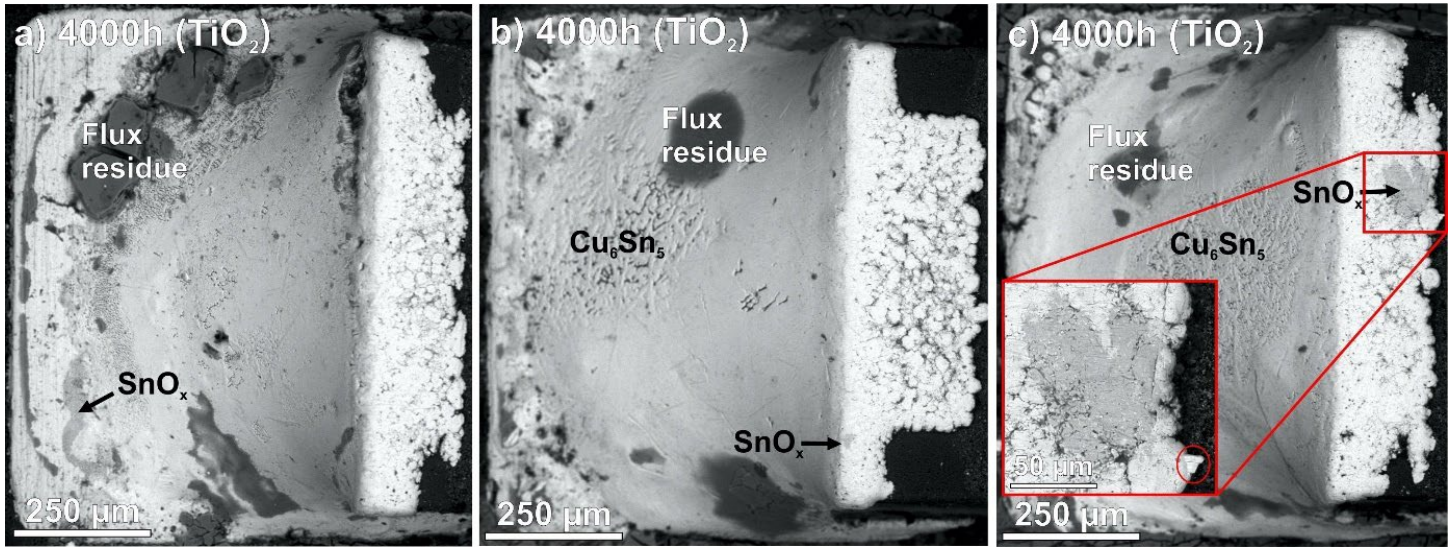




Reliability results

SAC0307-TiO2 after 4000h*: TiO_2 NPs can improve the corrosion resistance of SAC alloys and suppress Sn whisker growth.

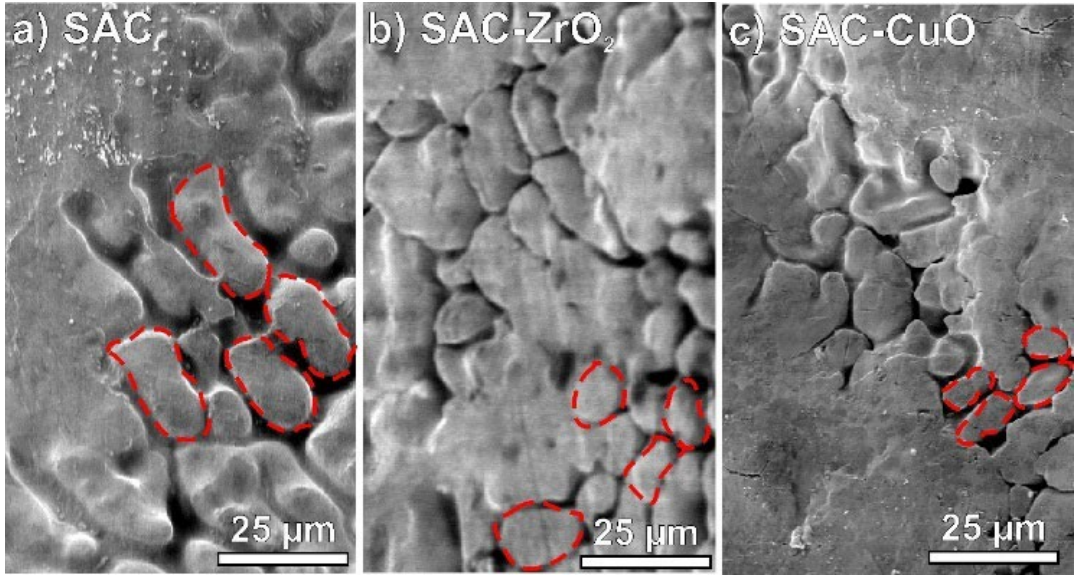
*B. Illés et al. Suppression of Sn whisker growth from SnAgCu solder alloy with TiO_2 and ZnO reinforcement nano-particles by increasing the corrosion resistance of the composite alloy, J. Mater. Res. Tech. 20 (2022) 4231-4240.



Discussion

Sn grain refinement in composite solder joints:

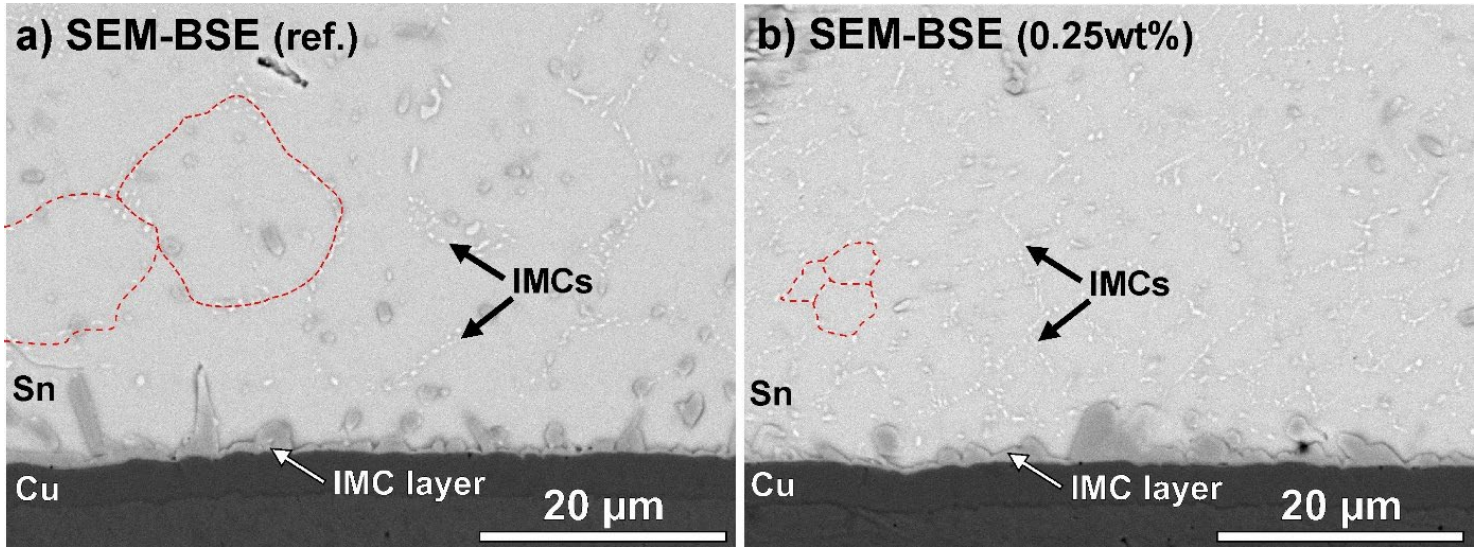
- Sn grains were visible on the surface of the solder joint.
- „Rough comparison”:
  - ref. SAC - 20-25 µm,
  - SAC-ZrO2 - 15-20 µm,
  - SAC-CuO - 10-15 µm.
- Measurements on mechanical cross-sections are necessary.



Discussion

Sn grain refinement in composite solder joints: TiO_2 NPs can considerably refine the Sn gran structure*.

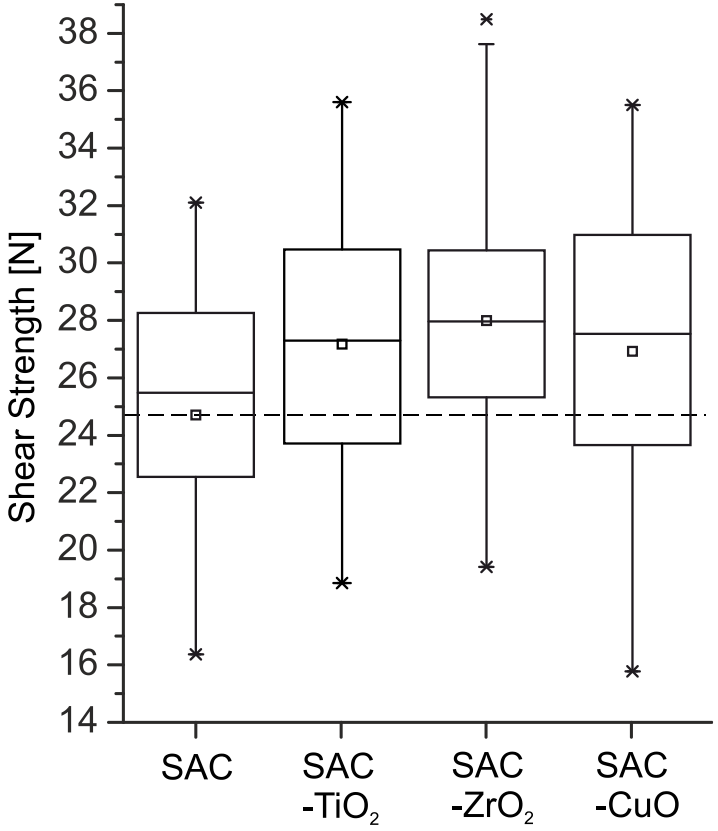
*B. Illés et al., Incorporation and corrosion protection mechanism of TiO2 nano-particles in SnAgCu composite alloys: experimental and density functional theory study, Ceramic. Int. 49 (2023) 23765-23774.



Discussion

Sn grain refinement in composite solder joints:

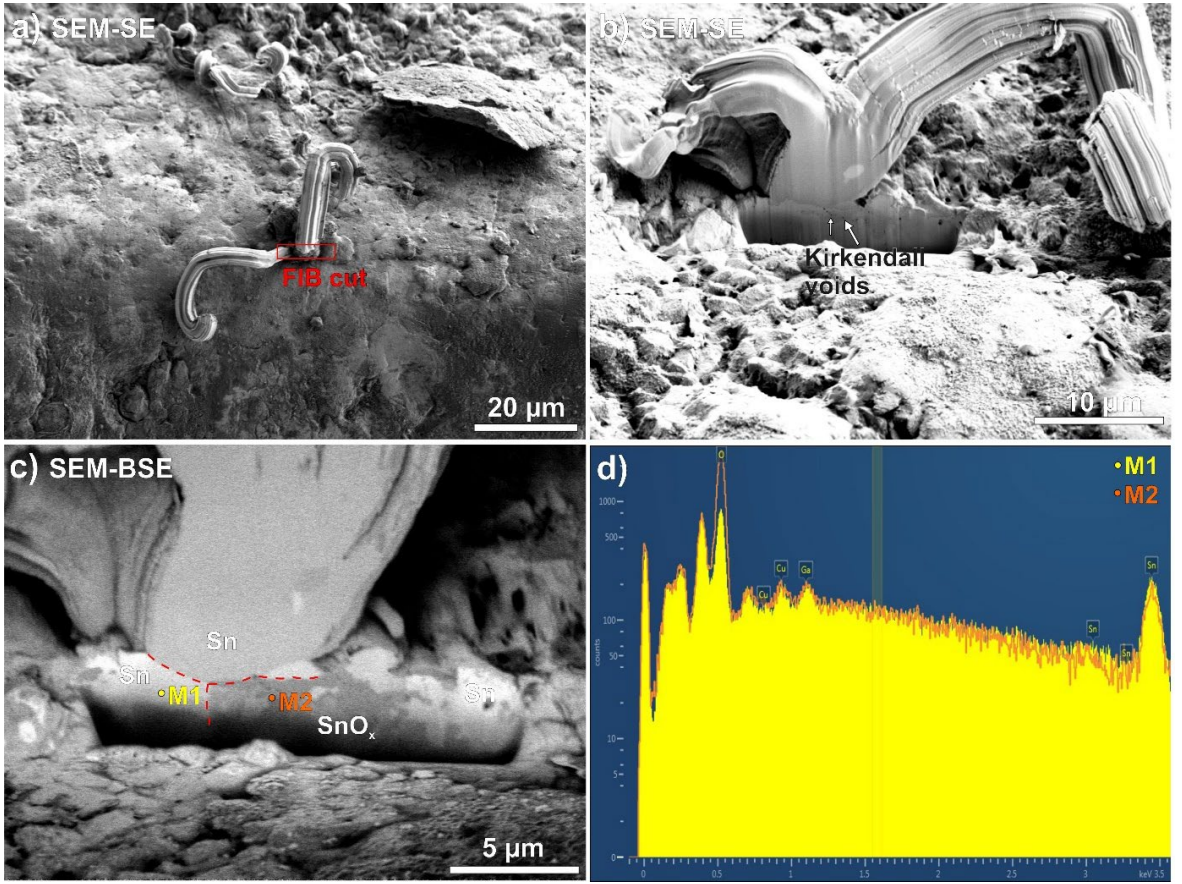
- Shear strength improvement of the nano-composite solder joints was caused by the dispersion-strengthening mechanisms (finer grain structure).
- ***Whiskers?***



Discussion

FIB cut of a whisker couple*:

- ***Corroded Sn grain under the whiskers.***



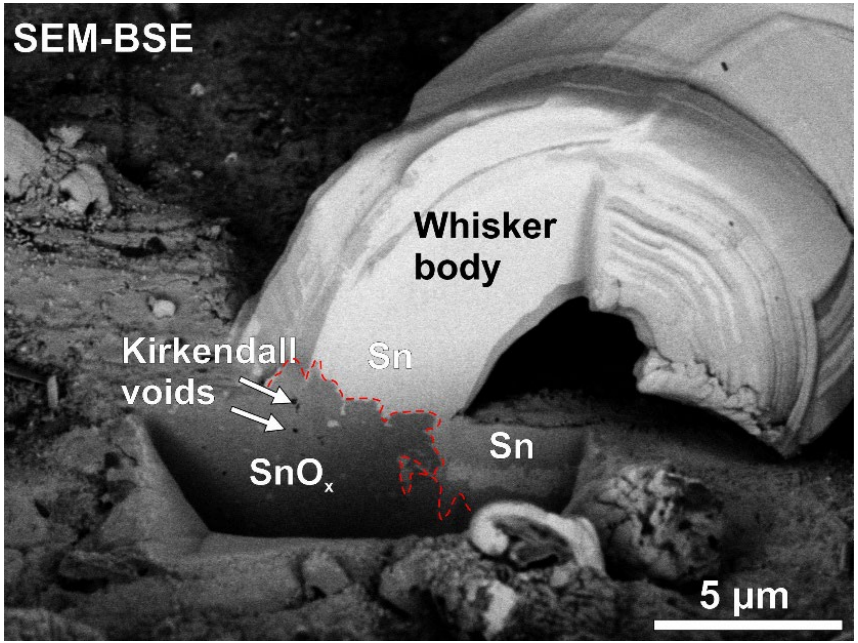
* B. Illés, et. al, Suppression of Sn whisker growth from SnAgCu solder alloy with TiO2 and ZnO reinforcement nano-particles by increasing the corrosion resistance of the composite alloy, J. Mater Res. Tech. 20 (2022) 4231-4240

Discussion

Corrosion induced Sn whisker growth:

- In a wet environment, electrochemical cells form
- ***Sn is anodic*** to the IMCs, mainly Sn will corrode.

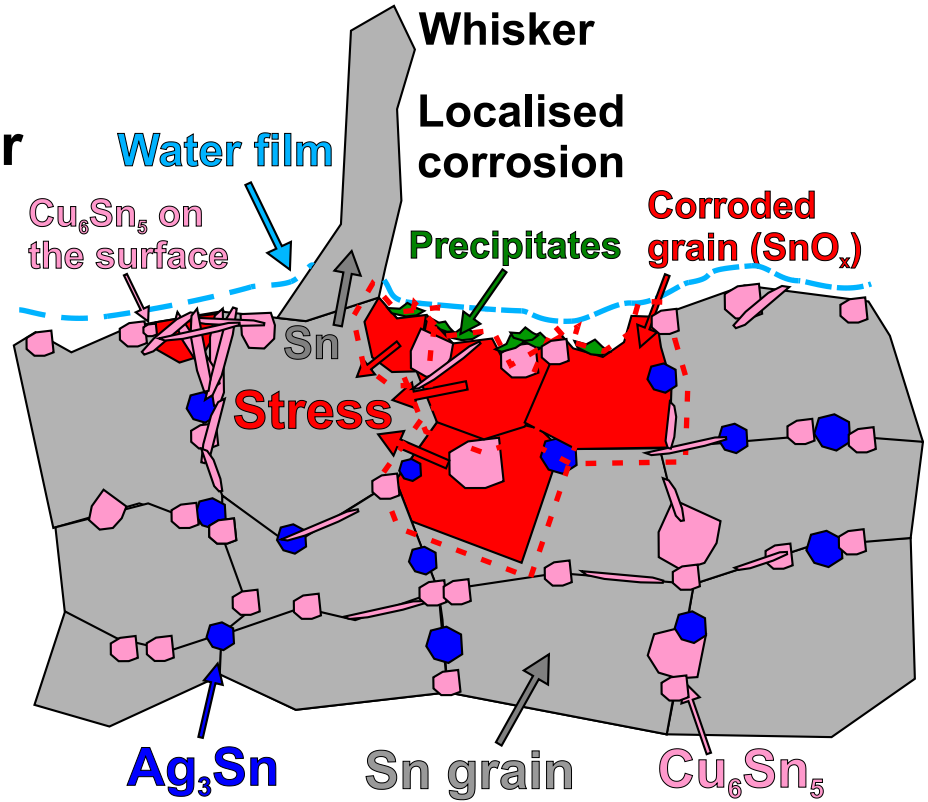
Oxide	Free energy of formation, ΔG^0 [kJ/mol]	Equilibrium potential [V]
SnO	-251.9	-0.7955
SnO_2	-515.8	-0.8266
$Sn(OH)_{2(aq)}$	-491.6	-0.8090
$Sn(OH)_{4(aq)}$	-994.9	-0.8406



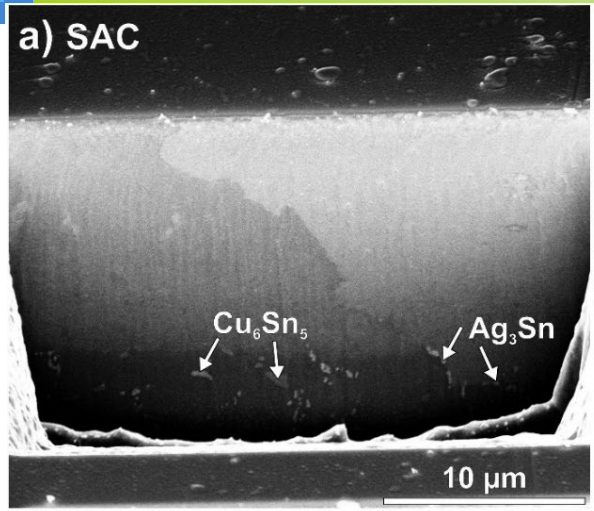
Discussion

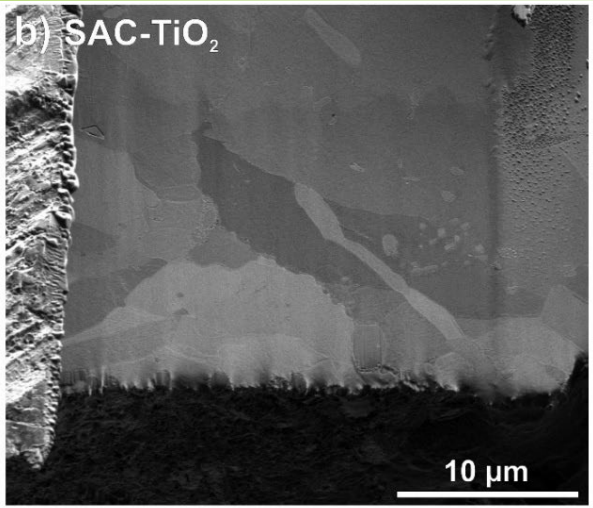
Corrosion induced Sn whisker growth:

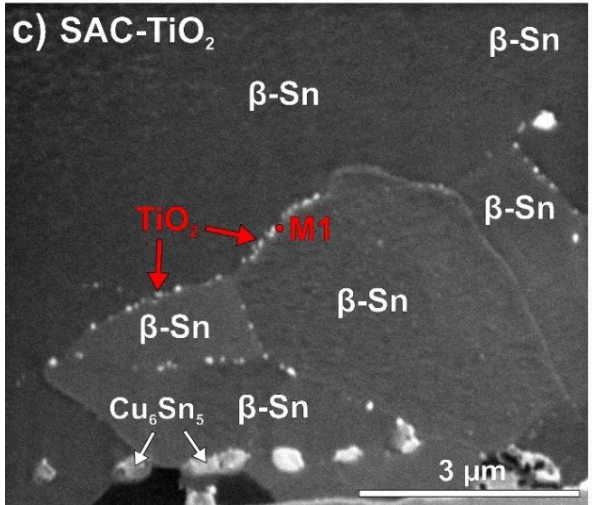
- ***Formation of SnO_x results in a volumetric increase***
- Volumetric increase causes a ***mechanical stress.***
- Mechanical stress is relaxed by ***whisker growth.***

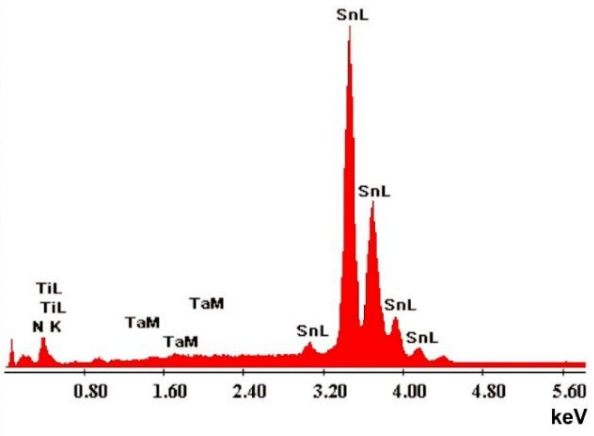


- *B. Illés et al., Incorporation and corrosion protection mechanism of TiO2 nano-particles in SnAgCu composite alloys: experimental and density functional theory study, Ceram. Inter. (2023) 23765-23774.







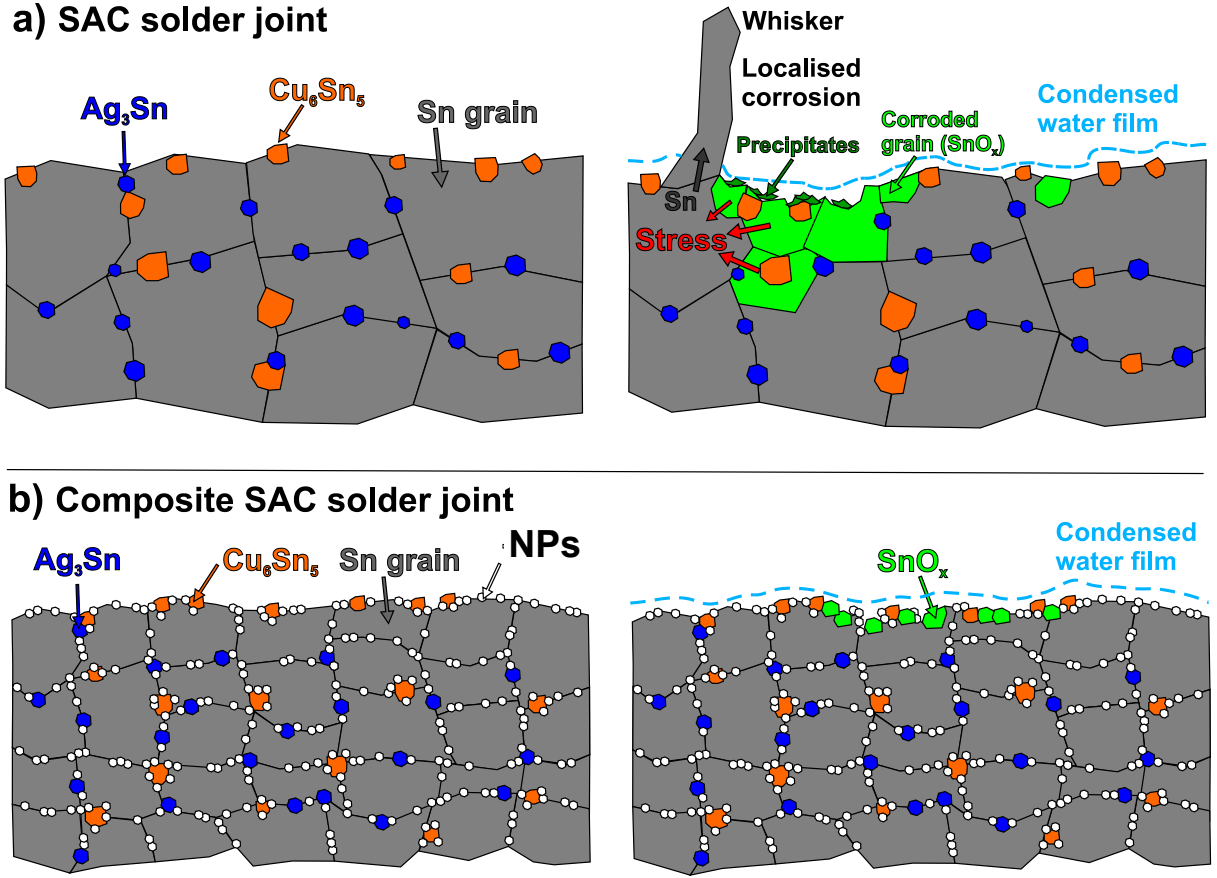


- ***Incorporated TiO_2 NPs at the Sn grain boundaries***
- Not soluble NPs segregated to the grain boundaries
- ***Protective TiO_2 layer forms at the grain boundaries.***

Discussion

Corrosion effect of NPs:

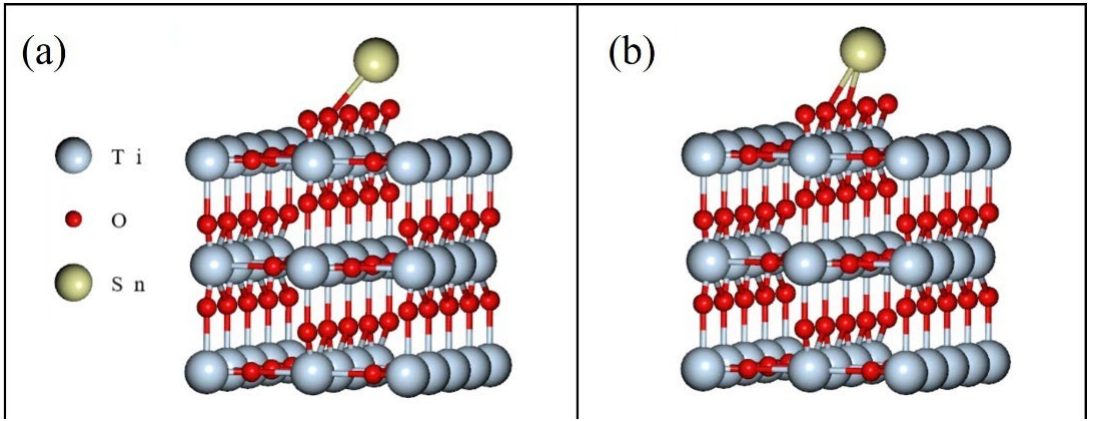
- TiO_2 positive
- ZrO_2 may be positive?
- CuO negative!



Discussion

Corrosion effect of NPs:

- TiO_2=Sn bonding is possible (according to DFT calculations)*
- ZrO_2=Sn? (in progress)
- CuO is not stable it can corrode further?



*B. Illés et al., Incorporation and corrosion protection mechanism of TiO2 nano-particles in SnAgCu composite alloys: experimental and density functional theory study, Ceram. Inter. (2023) 23765-23774.

Conclusions

- The NPs slightly decreased the wettability of nano-composite solder alloys.
- The NPs increased the average shear strength by 9-13% by the Sn grain refinement.
- TiO_2 considerably increased the corrosion resistance, ZrO_2 did not change significantly, and CuO decreased it.
- The solder joints produced Sn whiskers due to the corrosion caused mechanical stress in the joints.

Conclusions

- The amount of the Sn whiskers was in strong correlation with corrosion resistance of the solder joints.
- TiO_2 is still the most prospective candidate for composite soldering, both from the quality and reliability aspects of the solder joints.
- ZrO_2 increased the mechanical stability and performed the same reliability as reference SAC.
- CuO increased the mechanical stability, but it decreased their corrosion resistance.

THANK YOU!

- **illes.balazs@vik.bme.hu**

- Acknowledgement: This work was supported by the National Science Center Poland (NCN) project no. 2022/47/B/ST5/00997.