Comparative routes of solid-solution-formation by MM of Ag-70Cu (at%)

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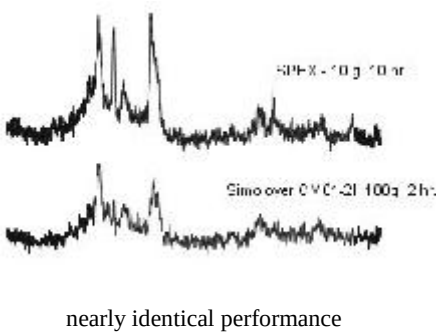
Abstract:

The solid-solution-formation (SSF) of Ag-70Cu (at%) has been chosen as the goal to be achieved by Mechanical Milling (MM) in a SPEX8000D-Mixer/mill and alternatively by a Simoloyer CM01-2l. In case of the SPEX-Mixer/mill, this is reached after about 43.2 ks, in case of the Simoloyer after 18 ks.
The observation, that processing at given parameters in the Simoloyer leads to a flaky geometry already after 0.060 ks versus the SPEX-Mixer/mill after 10.8 ks or not at all is concluded to be caused by a higher collision rate. In result this matches to the long known attempt, that the collision itself is the main event for energy transfer in MA. Additionally in case of the Simoloyer, Cycle Operation has been applied which results here in rapid flaking with quasi-disappearing ductility followed by shear-stress to break the flaky structure repeatedly.
Since a higher collision rate versus shear and friction effect is expected to cause less abrasive wear on the milling tools, the Fe-contamination of both systems was investigated and showed a lower contamination for the Simoloyer which matches to the expectation, too.
Material's characterization is given by SEM, XRD and TEM.

1. Introduction

The aim of the present paper is to compare alternative routes of Mechanical Milling (MM) to achieve solid solution formation (SSF) in the example of Ag-70Cu (at%) by using different devices (Simoloyer and SPEX-Mixer/mill) with different kinetic energy impact levels.
In case of the Simoloyer, we did not use HKP (High Kinetic Processing) which would refer to a relative velocity of grinding media in the order of 9 m/s and higher but medium kinetic processing in the order of 4 m/s since the kinetic in the SPEX-Mixer/mill was expected to be around or below that level.
The Ag-Cu-system is attractive to investigate SSF by alternative MM-routes since it was one of the first systems studied by Mechanical Alloying (MA) and is perfectly defined by low energy milling and has perfectly been characterized [1-3]. It is a system very noble and easy to work with when a matter of comparison wants to be made. SSF is favoured because Cu and Ag belong to the same group in the periodic table. On the other hand, Ag and Cu do not form a SS in conventional melting route because of their significantly different atomic radii. Finally we can expect high deformation rates at relatively low sheer stress due to the fcc-structure of both of the materials which is expected to favour the SSF by quasi-thin-layer formation on micro-structural base.
The comparison of Simoloyer and SPEX-Mixer/mill is interesting because their have up to now not been any direct comparative investigation been reported. This has been done for Simoloyer and Planetary Ballmill [4] but for the theme here, all known data is confidential since this is always related to the scale-up res. to the commercialization of some advanced materials in industry. And of course the major issue is here, that the SPEX-mixer/mill cannot be scaled up at all due to strict technological barriers and in so far is limited to 5-10 g with powder yields usually at less than 50 %. That means any kind of direct application of results achieved by the SPEX-mixer/mill is impossible. On the other hand, a number of scientists are and/or have been using this device for fundamental research and in so far it is attractive to be able to determine potential relations of scalability by the Simoloyer for materials systems that fundamentally already exist.
In the following, we give one of these "blue" examples where we have been confirmed in 2002, to report some limited information about the initial phase of a scale up of a metal-matrix-battery-material

by a US-company where we neither can give the company-name, nor the composition of the MMC nor the pattern-scales of the given XRD-results. Figure 1a gives 2 XRD-patterns of the MMC with the received statement that the material referred to the upper pattern has been synthesized in a SPEX8000D-Mixer/mill in a processing time of 10 h at a batch of 10 g and the lower pattern refers to the same material but produced in a CM01-Simoloyer in a processing time of 2 h at a batch of 100 g where the XRD-investigation is reported to exhibit nearly identical performance. This information came along with 2 pictures of the two different devices being used where figure 1b shows the SPEX-Mixer/mill and figure 1c the laboratory-scale Simoloyer at this company.



nearly identical performance

Figure 1: XRD-patterns of MMC (a), SPEX8000D-Mixer/mill (b), laboratory-scale Simoloyer CM01-2l (c)

What makes the Simoloyer interesting here, is the high kinetic process (HKP) based not on shear and friction (low kinetic processing) but mainly on the collision of grinding media at relative velocities up to 14 m/s [5-6] which first promises a high level of energy impact and second a lower level of impurities res. of contamination by the milling tools since collision is naturally less abrasive than shear and friction effects. The systems are available in large scale of several hundred liters volume and are economically and ecologically favorable in particular in case they can be operated semi-automatically if they are combined with a continuous or semi-continuous (auto-batch) powder separation system [7-8]. Atmosphere and cooling seems non-problematic since these mills can be operated, loaded and unloaded under vacuum or inert gas and are equipped with efficient cooling or cooling and heating systems. Figure 2a shows an industrial-scale CM100-Simoloyer that is used for the processing of nanocrystalline metal-hydride and zinc-oxide, figure 2b the same size but in semi-continuously mode used for the processing of ductile metal flakes (Cu and Ag) [9-10].

Figure 2: Simoloyer CM100 at IREQ-Hydro Quebec / HERA Hydrogen (a) and at Fukuda Co. (b)

2. Experimental

2.1 Ag- and Cu-powder

Comparatively, the MM-process was applied in both, in a SPEX-Mixer/mill and in a Simoloyer (see chapter 1) to the Ag-Cu powder-mixture where the detailed composition is given in table 1. Both of the starting materials were based on the chemical production route and therefore of high purity.

starting powder mixture for the MM-process				
element	purity [%]	PS [µm]	comp. [at%]	comp. [wt%]
Ag	99.9	1-10	bal.	bal.
Cu	99.5	1-5	70	57.88

Table 1: Ag-Cu-starting powder mixture

In case of the SPEX-Mixer/mill, Methanol was used as a PCA in order to avoid sticking and agglomeration of the powder. In case of the Simoloyer, a PCA was not expected to be necessary since Cycle Operation [10-14] was applied. In both devices, MM was performed under argon-atmosphere which means in case of the SPEX-Mixer/mill, the vial was loaded in a glove-box and in case of the Simoloyer, a standard air-lock was used to transfer the starting powders from an argon-container into the evacuated grinding chamber which was after that flooded with argon, to. Figure 3 shows a picture of the air-lock at the grinding chamber. Detailed parameters and procedure are given in chapter 2.2 res. 2.3.

2.2 MM-process in the SPEX-Mixer/mill

The principle of the SPEX-Mixer/mill is, that a small milling vial is manually loaded with some grinding media (1-10 pieces) and powder (5-10 g) and this container will shake on an angle-section for and back. In this kinetic system, it is very difficult to determine the kinetic and no model was found. The interaction of grinding media can be imagined as the grinding media is driven by the moving vessel and always at that moment, when the vessel is changing the direction, the milling balls that follow the container with time delay are hit by the vessel and accelerated into the vice-versa direction. If a number of balls is used, collision will take place in the hit front of the imagined ball-packet and shear and friction effects are initiated in between the grinding media. However, if we take into account, that the angle of the shake-like motion describes only a distance of less than 20 mm, in other words the milling vial is only moving for 2 cm, then the SPEX-Mixer/mill turns out to be simply a kind of a vibration mill.
In the literature, a number for a velocity was found at 18 m/s [15] which must be regarded sceptical since it would not match at all to the numbers given at figure 1. Since XRD-investigation here is related to a kind of lattice-destruction, which is in the MM related directly to the kinetic of this process, it could not be explained, that a system at a maximum relative velocity of grinding media of 14 m/s would after 2 h lead to similar result than a system at a velocity of 18 m/s after 10 h.

process parameters of Ag-Cu-powder mixture in the SPEX-Mixer	
mixing/milling device	SPEX8000D-Mixer/mill
mixing/milling vessel	stainless steel, 80 cc approx.
grinding media	100Cr6, 6 mm
grinding media load	6 balls (30 g)
PCA (lubricant)	5 drops of Methanol
starting powder	Ag-70Cu (mixture by at%)
starting powder load	6 g
powder/ball weight ratio	1 : 5
atmosphere	Argon during loading
frequency	set by mixer-manufacturer, 5 hz approx.
MM time I - IV	10.8, 21.6, 43.2, 54.0, 75.6 ks (3-21 h)
milling temperature	< 50 °C (vessel outside, estimated)
average powder yield	approx. 3-4 g >> 50-65 %

Table 2: process parameters of Ag-Cu-powder mixture in the SPEX-Mixer/mill

If we follow the attempt to better compare the SPEX-mill with a vibration-mill, then the found number for the velocity must be regarded even more sceptical.

Figure 1b shows a picture of the SPEX8000D-Mixer/mill which is the same model that has been used here. In this device, MM was carried out for 10.8, 21.6, 43.2, 54 and 75.6 ks which refers to 3, 6, 12, 15 and 21 h respectively where the detailed process-parameters are given in table 2. For processing, the vessel of the mixer/mill is removed and carried into a glove-box in order to load and maintain the Ar-atmosphere in

the mixing/milling-vessel. Then it was returned to the mixer/mill for the MM. Problematic is the control of the milling temperature since there is no cooling system of the vial available. The only way is to cool the environment (e.g. to place the mill into a fridge or use a van).
After each of the MM-sequence, the vessel was transferred into a glove-box and powder and balls were unloaded onto a sieve in order to receive the powder only. Here it is of course very difficult to remove all of the powder, in particular because some of the material is sticking at the inner vessel-wall and at the milling balls. This is why the Methanol was used as a lubricant and by this method we could receive at least a powder yield of about 3-4 g which refers to 50-65 % approx.

2.3 MM-process in the Simoloyer

For the explanation of the Simoloyer as a horizontal high energy ball mill we can refer to the introduction of this paper, where the same model (CM01-2lm) that has been used here is given in figure 1c already. The Simoloyer devices are known from academic as well as industrial applications in MA [16-17], high energy milling (HEM) [7-10] and reactive milling (RM) [14, 18-19] and supply the highest relative velocity of grinding media, which leads to a high level of kinetic energy transfer, an intensive grinding effect and short processing times. Since the grinding media is accelerated by a horizontally arranged rotor inside the grinding vessel, these devices do not have to move unnecessarily any large masses like e.g. the entire chamber/mill in case of vibration-, shaker- or planetary ballmills.

Figure 3: collision effects in HKP (Simoloyer)

Figure 3 shows a real image of a horizontal high energy ball mill in operation where the effect of collision in MM is visualized and the working principle can be imagined where the rotor is the tool to transfer the kinetic energy into the grinding media and the grinding media transfers into the powder material. The Simoloyer CM01-2l can be operated at rotation frequencies up to 1800 rpm, is water-cooled and computer-operated. This laboratory-scale size has been used for the MM at medium kinetic and was carried out for 3.6, 7.2, 10.8, 14.4, 18.0 and 25.2 ks which refers to 1, 2, 3, 4, 5 and 7 hours which is quite long for the Simoloyer but was set since the kinetic was decided to be used at a quite low level in the range of 600 rpm which refers to 3.6 m/s only. In maximum this was still 3 times shorter than in case of the SPEX-Mixer/mill since still a higher efficiency was expected. Since the definition of high kinetic processing (HKP) requires a relative velocity of grinding media higher than 9-10 m/s, here we might want to talk about medium kinetic processing (MKP). The detailed process-parameters are given in table 3.

process parameters of Ag-Cu-powder mixture in the Simoloyer	
milling device	Simoloyer CM01, 2.7 kW,
operating software	Maltoz 3.1
grinding unit	W01-2l (2 liter, water-cooled)
grinding media	Chromium steel, 100Cr6, 5 mm, 1.5 kg
PCA (lubricant)	no > Cycle Operation
starting powder	Ag-70Cu (mixture by at%)
starting powder load	30 g
powder/ball weight ratio	1:50
atmosphere	Argon, preceding evacuation
Operation Cycle	600/150 rpm - 14/1 min (refers to 3.6 m/s)
Discharging Cycle	150/600 rpm - 4/1 min
average discharging time	10-20 min
MM time I - VI	3.6, 7.2, 10.8, 14.4, 18.0, 25.2 ks (1-7 h)
milling temperature	< 25 °C (vessel inside by Maltoz)
feeding system	standard air-lock DN40-KF
discharging/separation	draingrating Ask-01
average powder yield	approx. 27-31 g >> 90-103 %

Table 3: process parameters of Ag-Cu-powder mixture in the Simoloyer

In order to not to change the load-relations inside the chamber, we did not use the sampling-unit which means for each MM-sequence, a separate MM-process was operated. For loading the starting powder, first the mill that must be in charging/operation position is evacuated to around 10^{-4} hPa and then flooded with Argon. The powder, that was loaded inside a glove-box into a powder-container, was transferred by the air-lock into the vessel at the same time when the vacuum was flooded since then the gas flow can even be used for the powder transportation.

After the adjusted MM-time elapsed, the grinding unit is tuned into discharging position and the same air-lock (after cleaning) was used for unloading the powder where this time first the powder container is evacuated via the air-lock. In that way, the gas-flow supported the unloading (a little) and the powder was discharged completely (grinding media remains in vessel).
Unloading is computerized and automatically operated. In order to increase the powder yield and to decrease the discharging time, Cycle Operation (figure 4) has been applied which means during discharging, the rotational speed of the rotor is changed in a special frequency in the range from here 150-600 rpm which has been proven to tremendously increase the powder yield of materials that tend to stick and agglomerate under MM to the milling tools and to each other [10-14].

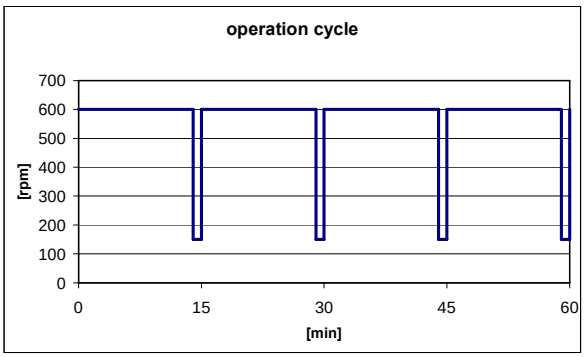


Figure 4: Operation Cycle for MM

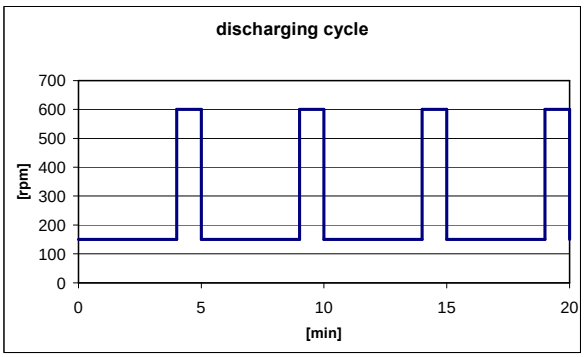


Figure 5: Discharging Cycle after MM

By this method in average complete powder yield could be obtained. Since between the each of the different MM-operations, the system has never been opened and since a little amount of powder always remains in the system e.g. sticking to grinding balls and vessel, the powder yield varied between 90 and 103 % after Discharging-Cycle of 10-20 min at 150/600 rpm (figure 5). Both of the cooling systems (vessel and pre-seal-unit) were constantly operated and the computerized measurement of the inner-vessel surface indicated temperatures lower than 25°C.

2.4 powder characterization

The initial and the as milled powders were characterized by SEM, XRD and TEM.
For Scanning Electron Microscopy, we applied a Jeol JSM-6300 and prepared the powder samples on a graphite tape in order to observe morphology and size. The iron-contamination of the powder samples has been investigated by Microanalysis using the same device. For X-ray diffraction we applied a Siemens Diffractometer D 5000 using monochromatic Cu-Kα radiation and determined/estimated the grain size by the Scherrer method and later confirmed by TEM. For Transmission Electron Microscopy we applied a Jeol JSM 2000 FXII and used an ultrasonic bath to de-agglomerate the powder samples and then mounted on copper grids.

3. Results

3.1 SEM and Microanalysis

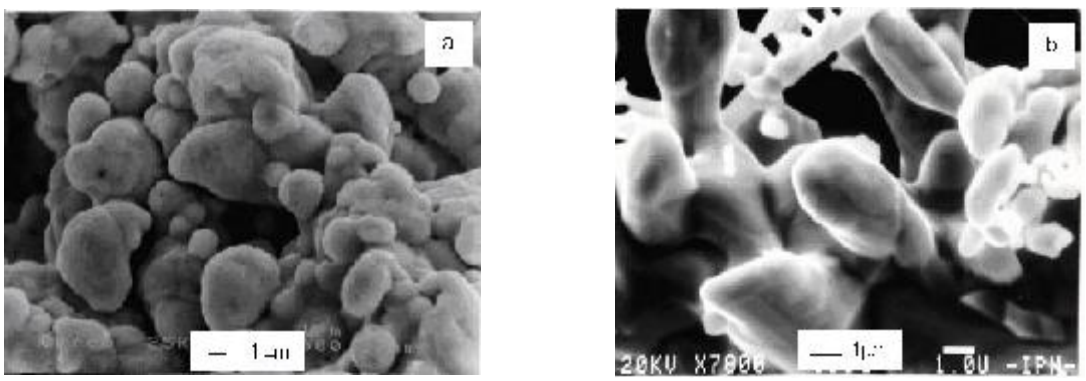


Figure 6: SEM-micrographs of the starting powders (a) Cu and (b) Ag

Figures 6a and 6b show the SEM-micrographs of the starting powders (a) Cu and (b) Ag.
Copper presents rounded shape with some porosity and an average particle size of around 5 µm, Silver shows an elongated shape with an average particle size between 1-10 µm.

Figures 7a-e gives the SEM-micrographs of processed powder by the SPEX-Mixer/mill after 10.8, 21.6, 43.2, 54 and 75.6 ks respectively.
After 10.8 ks a flattened shape of the particles can be observed where the flattening seems to increase until that point when the image after 43.1 ks was obtained. After 21.6 ks, the primary particles appear as a kind of multi-layer agglomerates which looks alike until 54 ks. As of 75.6 ks, the primary particles look more like fissured bulks of agglomerates with irregular shape and not flake-like.

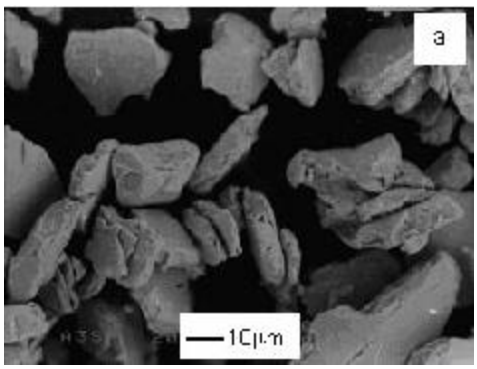


Fig. 7a (Ag-70Cu after 10.8 ks)

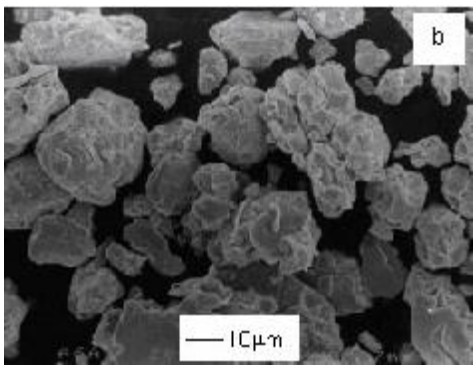


Fig. 7b (Ag-70Cu after 21.6 ks)

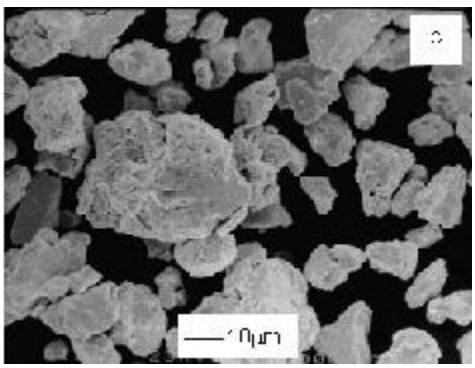


Fig. 7c (Ag-70Cu after 43.2 ks)

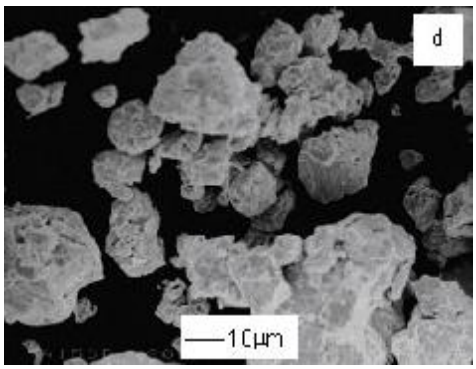


Fig. 7d (Ag-70Cu after 54.0 ks)

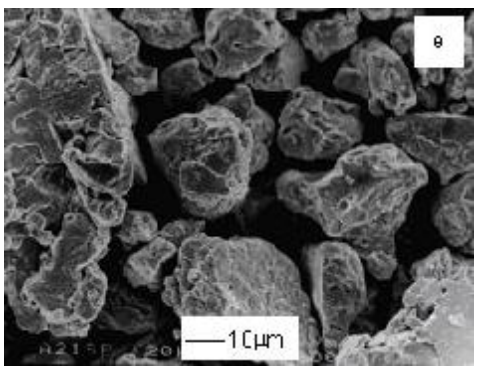


Fig. 7e (Ag-70Cu after 75.6 ks)

Figure 7: SEM-micrographs of Ag-70Cu powders after MM in the SPEX-Mixer/mill at various times

The most close to flaky-structure seems to appear on the image obtained after 43.2 ks and the thickness is carefully estimated to an average of maybe 5-10 µm at an average particle size of around 10-40 µm.

In table 4 we try to summarize the above where we estimate the morphology evolution, the average particle size and in case of flaky structure the thickness of the particles:

SEM-results related to morphology evolution after MM in the SPEX-Mixer/mill, estimates				
MM-time		particle shape	particle size	particle thickness
[ks]	[h]		[µm]	[µm]
0	0	spherical-elongated	1-10	
10.8	3	flattened bulks	30	5-10
21.6	6	thick flakes	30	5-10
43.2	12	flattened bulks	10-40	5-10
54.0	15	flattened bulks	10-30	
75.6	21	agglomerated bulks	20-100	

Table 4: summary of SEM-results related to morphology evolution after MM in the SPEX-Mixer/mill

Figures 8a-f gives the SEM-micrographs of processed powder by the Simoloyer after 3.6, 7.2, 10.8, 14.4, 18.0 and 25.2 ks respectively.

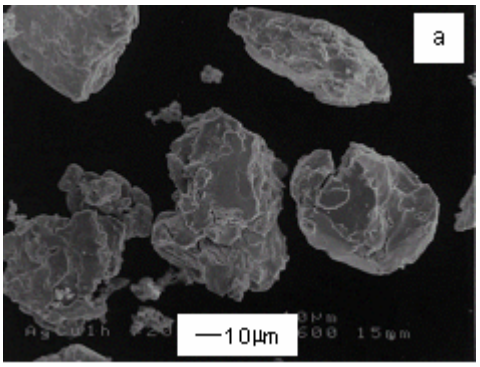


Fig. 8a (Ag-70Cu after 3.6 ks)

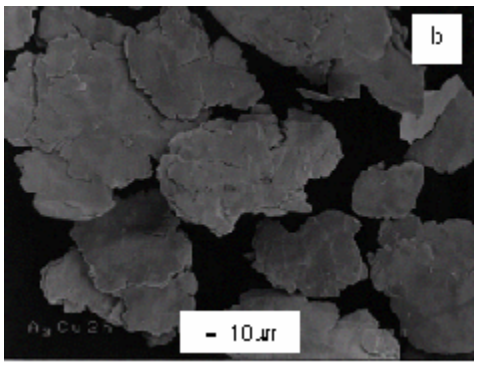


Fig. 8b (Ag-70Cu after 7.2 ks)

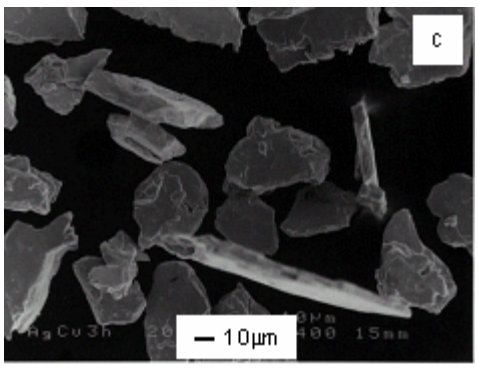


Fig. 8c (Ag-70Cu after 10.8 ks)

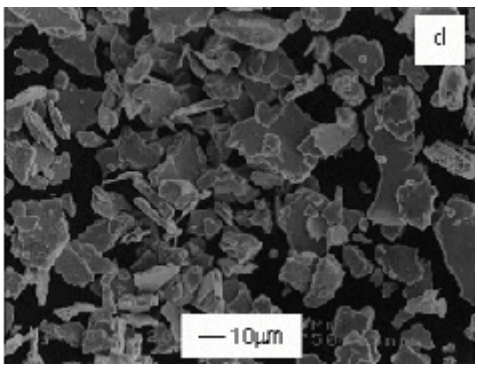


Fig. 8d (Ag-70Cu after 14.4 ks)

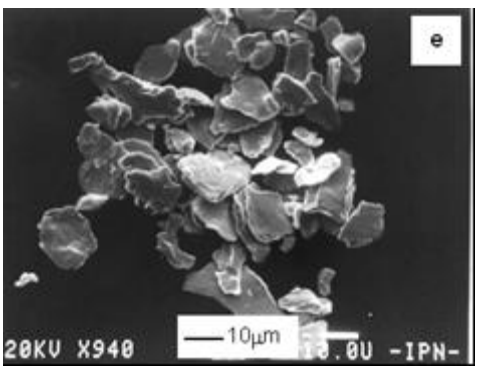


Fig. 8e (Ag-70Cu after 18.0 ks)

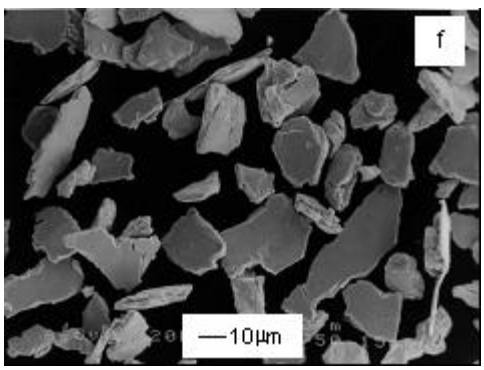


Fig. 8f (Ag-70Cu after 25.2 ks)

Figure 8: SEM-micrographs of Ag-70Cu powders after MM in the Simoloyer at various times

After 3.6 ks a very much flattened and in so far flaky shape appears and the primary particles look like a multi-layered agglomerate but much thinner than ever reached in the SPEX-Mixer/mill. The size can be estimated to an average of 60 µm. At 7.2 ks, the particles look much more condensed and the size got much larger up to more than 250 µm where the thickness is estimated to less than 5 µm. At 10.8 ks, the surface of the flaky bulks is smoother but the edges are still fissured and irregular where the thickness is estimated to about 5 µm and the size got smaller to an average of maybe 50-140 µm. At 18 ks, the morphology looks similar but the size is significantly smaller at an average of 20 µm. Also at 18 ks, the appearance remained similar and size further reduced to an average of maybe 10 µm. At 21.6 ks, the size seemed to slightly increase again and the surface appears much smoother. The edges always remain fissured.

In table 5 we try to summarize the above where we estimate the morphology evolution, the average particle size and in case of flaky structure the thickness of the particles:

SEM-results related to morphology evolution after MM in the Simoloyer, estimates				
MM-time		particle shape	particle size	particle thickness
[ks]	[h]		[µm]	[µm]
0	0	spherical-elongated	1-10	
3.6	1	thick flakes	60	5
7.2	2	thinner flakes	300	1-5
10.8	3	flaky fractures	50-140	5
14.4	4	flaky fractures	20	3-5
18.0	5	flaky fractures	10	3-5
25.2	7	flaky fractures	10-30	3-5

Table 5: summary of SEM-results related to morphology evolution after MM in the Simoloyer

The graph in figure 9 gives the results from the Fe-mapping which we achieved by microanalysis investigating at least 10 areas per spot. Remarkable is the fact, that even at the same processing times the Fe-contamination in case of MM in the SPEX-Mixer/mill is always 1.5-4 times higher.

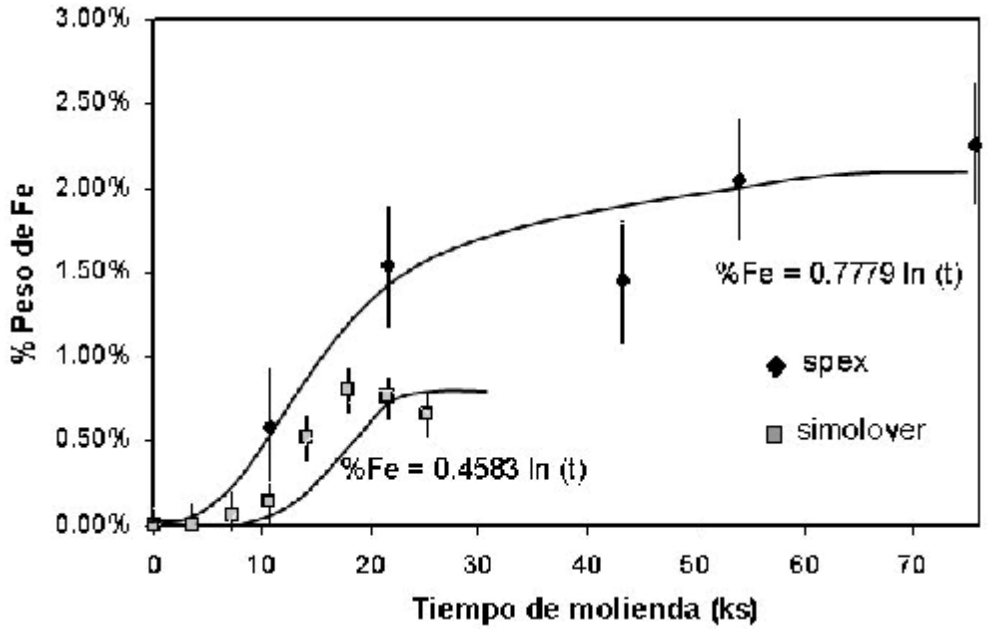


Figure 9: Fe-contamination by microanalysis

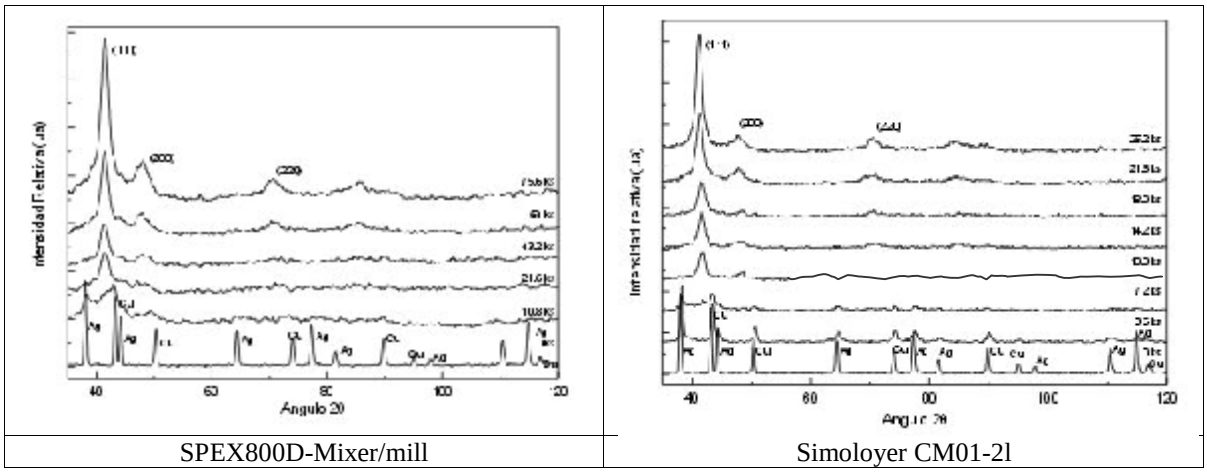
If we take a fix-point at that time when the SSF was observed, in case of the SPEX-Mixer/mill, the Fe-contamination is close to 2 % and in case of the Simoloyer 1.2 %. It seems, that in case of the Simoloyer, there is a time frame, where flaky structure is given already but Fe-contamination cannot be detected yet.

3.2 XRD-investigation

Figures 10a and 10b show the XRD-patterns of the original and the processed powders achieved (a) from the SPEX-Mixer/mill and (b) from the Simoloyer.

We determine the solid solution formation (SSF) by the detection of the (111), (200) and (220) planes of the SS. In case of the MM in the SPEX-Mixer/mill, this could be expected after 21.6 ks and including the later reported TEM-investigation, we can determine it to be obtained at nanometric grain size after 43.2 ks.

In case of the MM in the Simoloyer, this could be expected after 10.8/14.2 ks according to the XRD and including the TEM after 18 ks which is about 2.4 times faster. From angle measurement we calculated the lattice parameter in both cases to 3.769 Å.



SPEX800D-Mixer/mill | Simoloyer CM01-2l

Figure 10: XRD-patterns of original and processed powders achieved (a) from the SPEX-Mixer/mill and (b) from the Simoloyer

The grain size determined by the Scherrer-method is given at < 10 nm for both cases, the grain size determined by TEM at 5-50 nm for the SPEX-Mixer/mill-process and at 5-30 nm for the Simoloyer-process. The results are listed in table 6:

Results of XRD (and TEM) in survey			
processing device	SSF after	grain size by TEM	grain size by Scherrer
SPEX-Mixer/mill	43.2 ks	5-50 nm	< 10 nm
Simoloyer CM01	18 ks	5-30 nm	< 10 nm

Table 6: results of XRD (and TEM) in survey

3.3 TEM-investigation

Since there are natural doubts on the reliability of XRD for the completion of SSF, which is the goal in this work, because we might expect some local re-crystallisation by high energy impact (local heat) and XRD would not detect a weight fraction below 5-10 percent depending on the element, it was necessary to check SSF by TEM.

The TEM-investigation of the MM powders in the SPEX-Mixer/mill after 43.2 ks is given in figure 11a-c. The dark- and brightfield micrographs (a, b) show a grain size at around 5-50 nm where we obtained a value estimate of < 10 nm by the Scherrer-method.

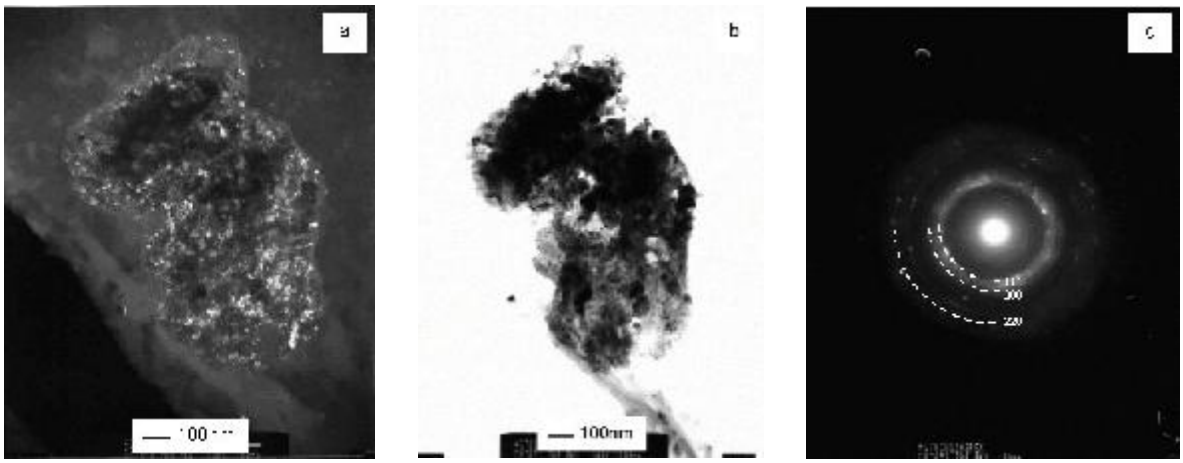


Figure 11: TEM-investigation of the MM powders in the SPEX-mill: (a) darkfield micrograph, (b) brightfield micrograph, (c) diffraction pattern after 43.2 ks

The diffraction pattern (c) shows the diffraction rings which are characteristic for the nanometric grains of the new solid solution formed. However, it seems, that the SSF has not yet been developed completely because according to our TEM-observation, there were still diffraction spots from Cu and Ag identified which can also be seen on figure 11c as spots out of the radii of the 111, 200 and 220 planes respectively.

The TEM-investigation of the MM powders in the Simoloyer after 18.0 ks is given in figure 12a-c.
The dark- and brightfield micrographs (a, b) show a grain size at around 5-30 nm where we obtained a value of 5 nm by the Scherrer-method.

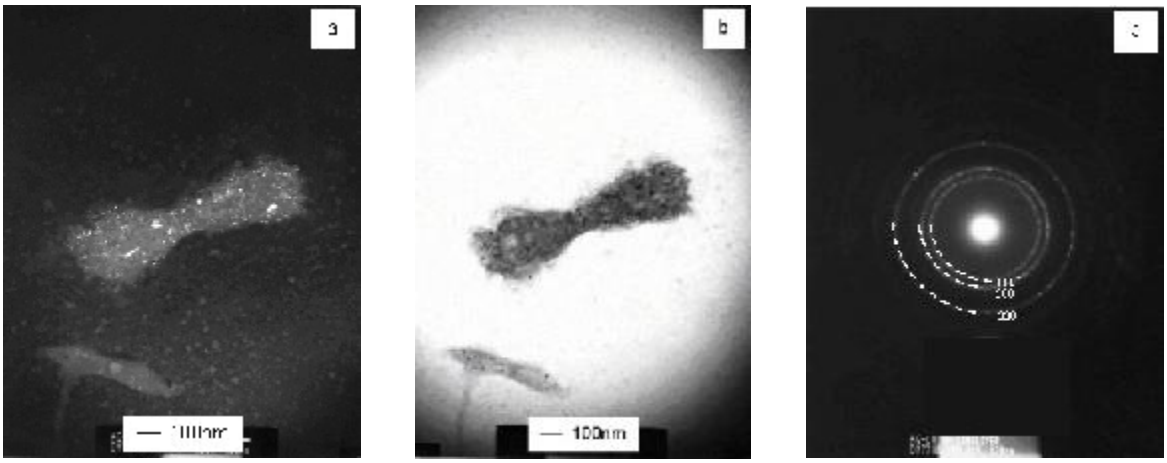


Figure 12: TEM-investigation of the MM powders in the Simoloyer: (a) darkfield micrograph, (b) brightfield micrograph, (c) diffraction pattern after 18.0 ks

The diffraction pattern (c) shows diffraction rings which are characteristic for the nanometric grains of the new solid solution formed.

Figure 13a-c shows the TEM-investigation of the MM powders in the Simoloyer after 14.4 ks. The dark- and brightfield micrographs (a, b) confirm a grain size at around 100-500 nm.

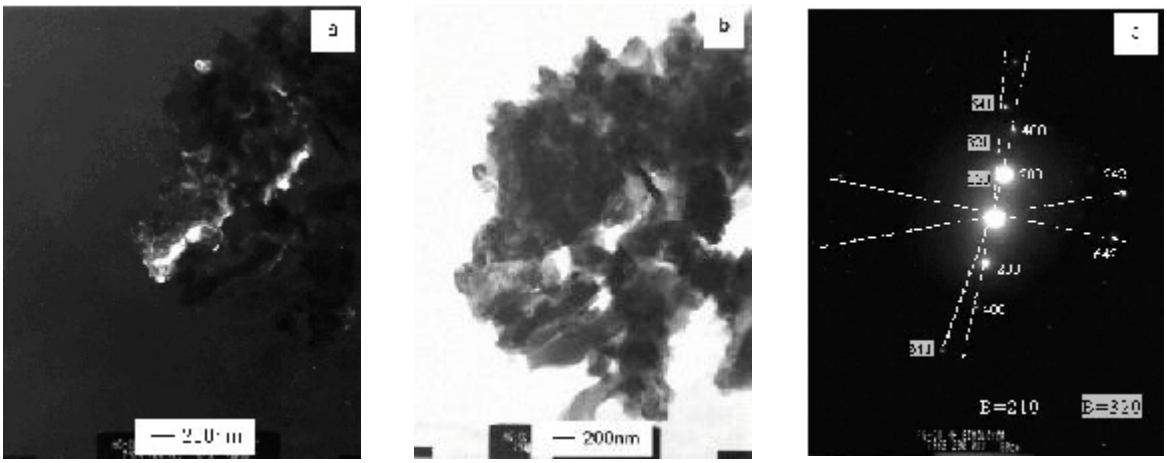


Figure 13: TEM-investigation of the MM powders in the Simoloyer: (a) darkfield micrograph, (b) brightfield micrograph, (c) diffraction pattern after 14.4 ks

The diffraction pattern (c) exhibits a dot-pattern that confirms microcrystalline grain size and was identified to belong to the SS of Cu and Ag. In result, at 14.4 ks, the SSF has already been obtained but a nanometric grain size was not achieved yet.

Figure 14a-c shows the TEM-investigation of the MM powders in the Simoloyer after 25.2 ks. The dark- and brightfield micrographs (a, b) confirm a grain size at around 100-500 nm.

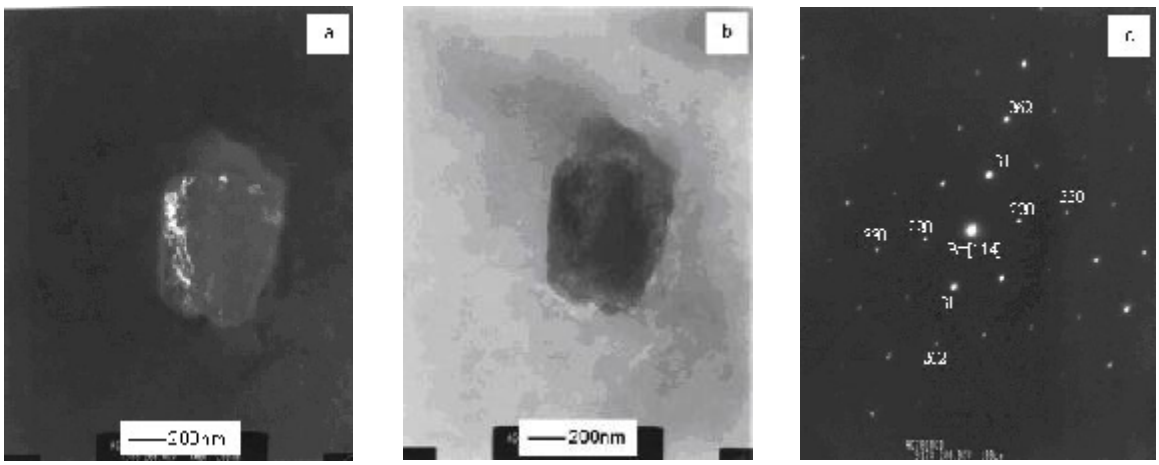


Figure 14: TEM-investigation of the MM powders in the Simoloyer: (a) darkfield micrograph, (b) brightfield micrograph, (c) diffraction pattern after 25.2 ks

The diffraction pattern (c) exhibits a spot-pattern that confirms grain growth of the SS which may be explained by to much energy impact into the material which is transformed into (micro-)heat.

4. SSF, Morphology evolution, Fe-contamination and MM-time

The comparison of the received results by microanalysis, XRD and TEM is given in table 7:

SEM-, XRD- and TEM-results (including microanalysis) in survey				
MM-device	SSF starts after	SSF completed after (b)	Fe-contamination after time b	comment
SPEX-Mixer/mill	21.6 ks	43.2 ks	1.9 wt %	3.8 x more Fe-contamination
Simoloyer	14.4 ks	18 ks	0.5 wt %	SSF achieved 2.4 x faster

Table 7: results of SEM-micrographs and microanalysis, XRD and TEM in survey

In result, the SSF is achieved in the Simoloyer 2.4 times faster at 3.8 times less Fe-contamination.
The comparison of the estimated morphology evolution based on the SEM-results (tables 4 and 5) is given in figure 15 where we additionally marked the SSF:

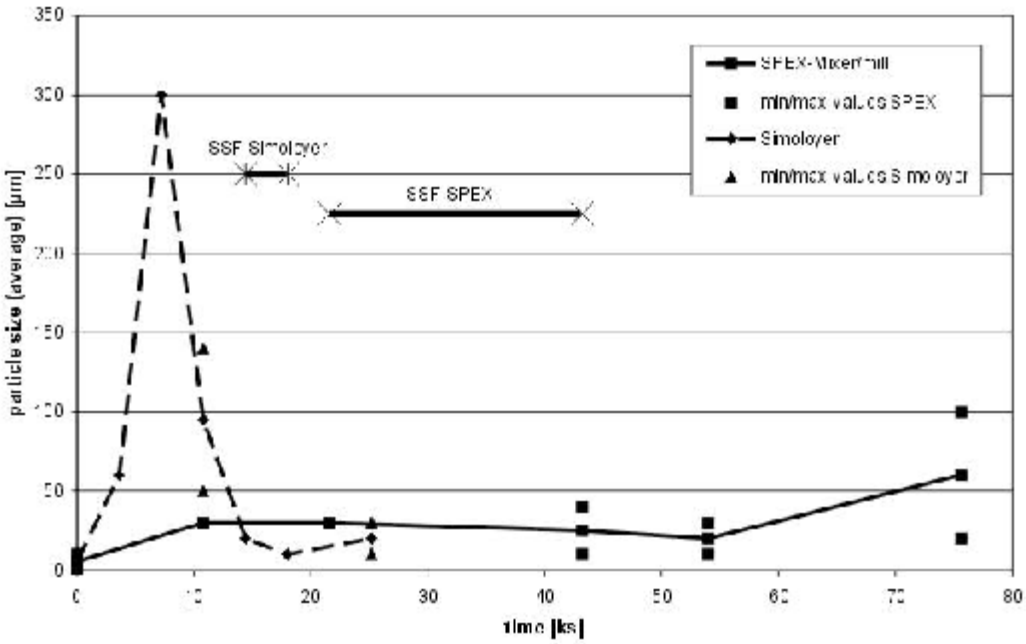


Figure 15: morphology evolution based on the SEM-results in survey

In figure 15 we can see impressively a major difference in the evolution. The tremendous increase of particle size in case of the Simoloyer identifies the formation of large flakes that later break into fractures. This does not happen in case of the SPEX-Mixer/mill where we assume that the kinetic here is to low and matches in so far to the hint that the SPEX-system can be better understood as a vibration mill rather than a system based on collision of grinding media (see chapter 2.2).
In order to further comment the morphology evolution in case of MM of Ag-70Cu as a mixture of ductile metals we refer for the initial morphology change to a parallel work [20]. Then we can predict the development as follows (table 8):

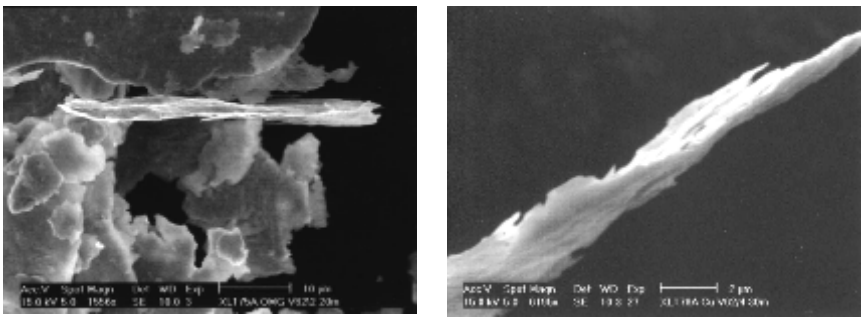
	Spex-Mixer/mill (low kinetic)		
		Simoloyer at medium kinetic (3.6 m/s)	
01	√	√	agglomeration of the starting powders to lose bulks
02	√	√	densification of still small loose bulks
03	√	√	flattening of the bulks to flaky shape, development of some large bulks
04	√	√	agglomeration of remains of stage 01 on the surface of flakes/large bulks
05		√	further flattening and break of the flaky bulks/flakes
06		√	repeat of stage 05 including cold-welding of flakes to bulks

Table 8: estimated morphology evolution in Spex-Mixer/mill and Simoloyer

The evolution stages 01-06 in table 8 give an attempt for the understanding of the formation of flakes when we process ductile metal powder by MM. Stages 05-06 seem not to apply for the process in the Spex-Mixer/mill since the kinetic is to low to create thin enough flakes with a work hardening effect.

We further assume that the initial flake formation, in particular if the flakes are built up by a multi-layer structure (of thinner flakes), does favor the SSF because for both transformations, the kinetic energy impact is determining [20-21].
Since in case of SSF, here, Ag-atoms shall be located in the Cu-lattice intersticially or by substitution, this is provided mainly by kinetic impact which means it is of major importance, how this kinetic impact can effect the lattice structure.
E.g. if some grinding media would be thrown into a volume of Ag-Cu-powder, there will be plastic deformation of the volume and there may be plastic deformation of some of the direct hit particles in the front-layer but it is very much unlikely, that this can cause atomic dislocations in the lattice of the materials. This means the dumping effect of the powder plays the same important role for SSF as well as for flake formation.

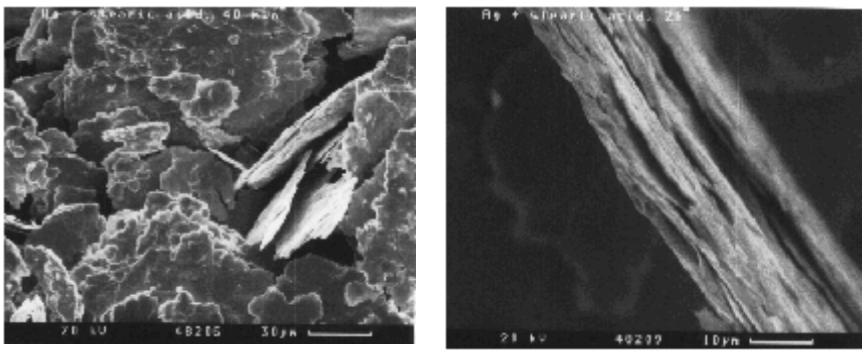
It must be pointed out again, that we used the Simoloyer only at medium kinetic (3.6 m/s) and not at high kinetic (> 9 m/s).
Since the SSF seems to and the flake-formation does depend on the kinetic energy impact, in the future, the work reported here shall be repeated with the Simoloyer not under medium kinetic at around 3.5 m/s but at high kinetic > 10 m/s. It has already been proved in earlier work [9-10, 22], that the formation of Ag- and Cu-flakes by HKP can be obtained already after some minutes processing time and at a flake-thickness less than 1 µm (figure 16 and 17 show SEM- and optical micrographs of Cu- and Ag-flakes that are produced at Zoz by HKP).
If we then take into account, that these flakes can be built up by a number of approximately 50 theoretical inter-layers according to the starting particle size [23], then we would end up with a theoretical thickness in 10 nm range.
If we apply this to a powder mixture and use the principle of MA and produce a kind of sandwich-structure, then we probably end up with very short diffusion ways inside this structure and this could explain why multi-layer flake formation favors SSF and it will be very interesting to find dependencies for this in the ongoing work where one of the next steps will be the application of HKP at 3-4 times higher relative velocities of the grinding media.



Picture (optical) of Cu-flake

Mr. Benz, please choose !

Figure 16: Zoz-Cu-flake Z-CUF17, (a, b) SEM- and (c) optical micrographs



Picture (optical) of Ag-flake

Mr. Benz, please choose !

Figure 17: Zoz-Ag-flake Z-AGF34, (a, b) SEM- and (b) optical micrographs

The given Cu- and Ag-flakes are manufactured under high kinetic in the Simoloyer at processing times below 30 minutes. The thickness is in average 3-5 times thinner that the thickness of the here processed Ag-70Cu-flakes at medium kinetic and at 5-40 times longer processing time also in the Simoloyer. Taking this into account, we can presume that the SSF at HKP will be obtained at much shorter processing time and will exhibit a much more flaky morphology.

5. Conclusions and References

Conclusions

The solid solution formation by MM of Ag-70Cu in the SPEX8000D-Mixer/mill after 43.2 ks and in the Simoloyer CM01-2l after 18 ks could be obtained at nanometric grain size.
For this, the Simoloyer was not used at high but at medium kinetic only (< 4 m/s).
After completion of the SSF, the Fe-contamination by the milling tools in the SPEX8000D-Mixer/mill was about 1.9 wt % and in the Simoloyer about 0.5 %.
It seems that the solid solution formation is related to flake like morphology which is achieved at shorter times in the Simoloyer.
It seems, that in case of the Simoloyer, there is a time frame, where flaky structure is given already but Fe-contamination cannot be detected yet.

In result, the Simoloyer-process leads to the SSF faster at lower contamination than the SPEX-Mixer/mill which should be understood as a vibrating mill rather than a high energy mill.

Most interesting will be the future work, when the Simoloyer will be used at high kinetic < 9 m/s.

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