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Microstructure and hardness development in a copper-nickel diffusion gradient model system

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Abstract. Cu has been electrolytically coated with Ni and subsequently deformed by rotary swaging up to a strain of $\epsilon=2$ to create a chemical gradient at the interface of the two elements. The extend of this chemical intermixing has been investigated through Energy Dispersive X-ray (EDX) spectroscopy in the Scanning and Transmission Electron Microscope (SEM and TEM). The depth, in which intermixing takes place, is about $1\mu\text{m}$ from the interface. Because of the uniform deformation, the structure does not get elongated but rather uniformly reduced in size. Microindentation hardness measurement shows a hardness increase from 120 to 135kp/mm^2 in the Cu phase with increasing strain. After annealing at 200°C for up to 4h the hardness first decreases, but raises above the value for the highly strained sample. The experimental findings are discussed with emphasis on surface mechanical alloying as a process of both scientific and technological interest.

1. Introduction

The modern world has a lot of requirements towards materials concerning strength, ductility, corrosion resistance, costs and often more like electrical conductivity or to be non-hazardous. Single unprocessed elements can often not fulfill these requirements, which is why new processing techniques, alloys and other material combinations are constantly developed to create hybrid materials [1-2]. This is an interesting way is to combine advanced processing techniques with the goal of at least partly alloying material together to make use of their traits but also creating a strong bonding between the two phases. Here we use the process of coating a metal onto another and deforming both of them to force the two metals to alloy thereby creating a chemical diffusion gradient. In one sample there will be different compositions of the two elements available while the whole sample will have received the same treatment. The coated and deformed samples can therefore be used as a modelsystem to investigate the microstructural effects depending on the different local alloying composition.

We have chosen to coat a Cu rod with Ni, since Cu and Ni form an intermixing crystal structure and can be alloyed together in every composition. This should make it easy to obtain a good bonding as well as induce a chemical interaction at the interface of Cu and Ni.

2. Experimental procedures

Ni was electrolytically coated onto Cu rods of 14mm diameter. The Cu rods were of commercial OFHC purity. The content of impurities is shown in table A of the appendix. Two levels of thickness of the coating were prepared. One with $50\mu\text{m}$ Ni coating around the rod and one with $1305\mu\text{m}$ Ni



coating. In both cases, the rods have been etched to increase the adhesion of the Ni coating on the Cu rod. Table B in the appendix shows the contents of the solution that has been used to coat the Ni onto the Cu rod while Table C shows the contents of the solution used to etch the rods before the coating.

Both samples (with 50 μ m coating and 1305 μ m coating) have been deformed afterwards by rotary swaging. Rotary swaging (RTS) has been chosen to deform the samples, as it ensures a uniform strain along the axes of the rod. The same process has also been chosen for fabricating Al-Cu clad composites as well [3]. Furthermore it introduces compressive strain in the swaged samples, which may improve properties under fatigue load, to be investigated. It consists of rotating hammers that leave a circular gap in the middle to insert the rod and that deform the rods perpendicular to the axis of the rod inserted. The hammers are exchangeable to allow different diameters of the gap and therefore different strain. Both samples were deformed in several passes with decreasing hammer diameter and therefore increasing strain. Table 1 shows the hammer diameter used and the resulting true strain as well as the temperature reached after each pass.

Table 1: Hammer diameter and resulting sample diameter used for deforming the Ni coated Cu rods. The strain is calculated by using equation (1) and the temperature was measured directly after each pass of swaging deformation by using a pyrometer.

Cu rod (50 μ m coating thickness)				
Swaging pass	Diameter mm	swaging block gap used / mm	True strain ϵ	Temperature $^{\circ}$ C
0	14.1		0	
1	13.06*	12.7	0.15	
2	11.67	11.3	0.38	30
3	10.2*	9.9	0.65	55
4	8.16	8	1.09	106
5	7.12*	7	1.37	78
6	6.09	6	1.68	90
7	5.66*	5.5	1.83	58

*Samples taken

Cu rod (1305 μ m coating thickness)				
Swaging pass	Diameter mm	swaging block gap used / mm	True strain ϵ	Temperature $^{\circ}$ C
0	16.61		0	
1	14.04	14.3	0.34	
2	13.1*	12.7	0.47	30
3	11.68	11.3	0.70	28
4	10.23*	9.9	0.97	40
5	8.23	8	1.40	138
6	7.16*	7	1.68	116
7	6.14	6	1.99	115
8	5.7*	5.5	2.14	70

*Samples taken

The true strain ϵ has been calculated from the initial diameter of the rod and the resulting diameter after each pass using equation (1):

$$\epsilon = \ln \left(\frac{s_0}{s_n} \right) \quad (1)$$

S_0 is the initial cross section and S_n is the measured cross section after each swaging pass. For the 50 μ m coated rod, samples have been cut after the 1st, 3rd, 5th and final 7th pass. For the 1305 μ m rod,

samples have been taken after the 2nd, 4th, 6th and final 8th pass to maintain comparable diameters of the samples.

These samples have been subjected to investigation by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and microhardness indentation.

3. Results and discussion

3.1. Chemical diffusion gradient

SEM scans have been taken on the samples in order to determine the thickness of the Ni phase after the swaging and also to investigate whether there have been cracks forming in one of the phases or the interfaces. Figure 1 shows an example for the 1305 μm coated Ni samples after 2, 4, 6 and 8 passes of swaging.

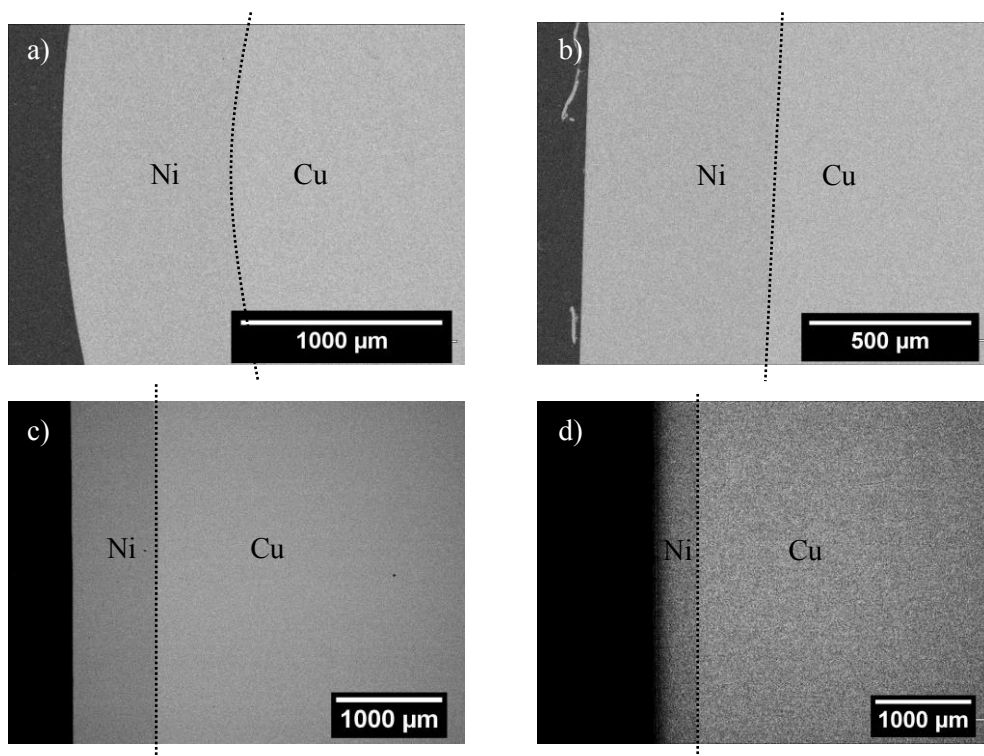


Figure 1. SEM images of the interface between the Cu core and the Ni coating after a) 2 passes ($\epsilon=0.47$), b) 4 passes ($\epsilon=0.97$), c) 6 passes ($\epsilon=1.68$) and d) 8 passes of swaging ($\epsilon=2.14$). The interface is marked with dotted line. There are no cracks visible at any of these stages both at the interface and within the core and the coating.

The SEM overview images show that the Ni coating decreases in thickness with increased number of swaging passes. This is expected as the total diameter of the coated rods decreases and instead elongates. No cracks were visible during the SEM investigation neither at the interface between the Cu core and the Ni coating, nor in the two phases itself.

Figures 2 and 3 show the results of an EDX scan over the Cu-Ni interface region of the 1305 μm sample after 2 and 8 passes.

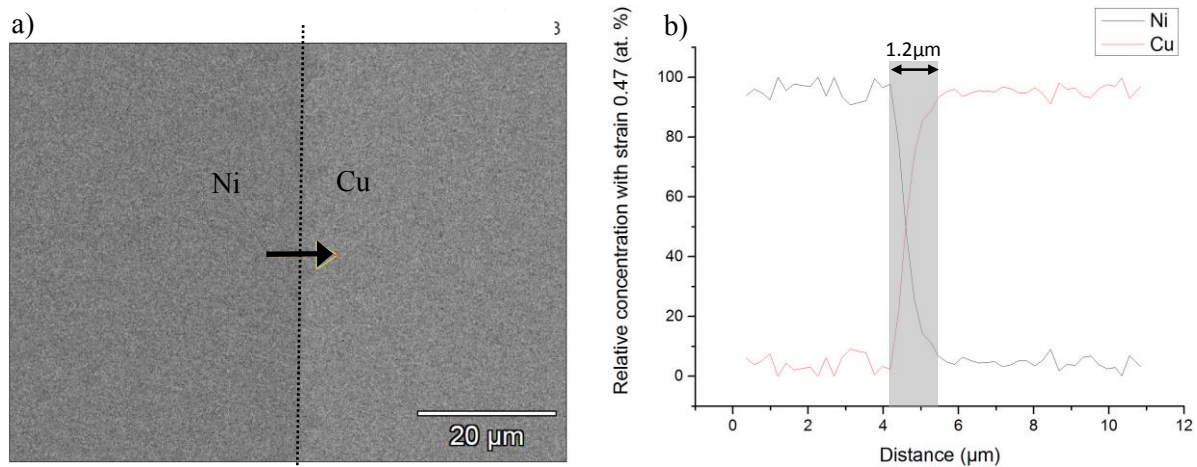


Figure 2. a) SEM image of the Ni-Cu interface region from the 1305 μ m coated sample after 2 passes of swaging ($\epsilon=0.47$) taken at 15kV. b) EDX scan over the line, marked with an arrow in a), showing the Ni and Cu content for each point in at.%.

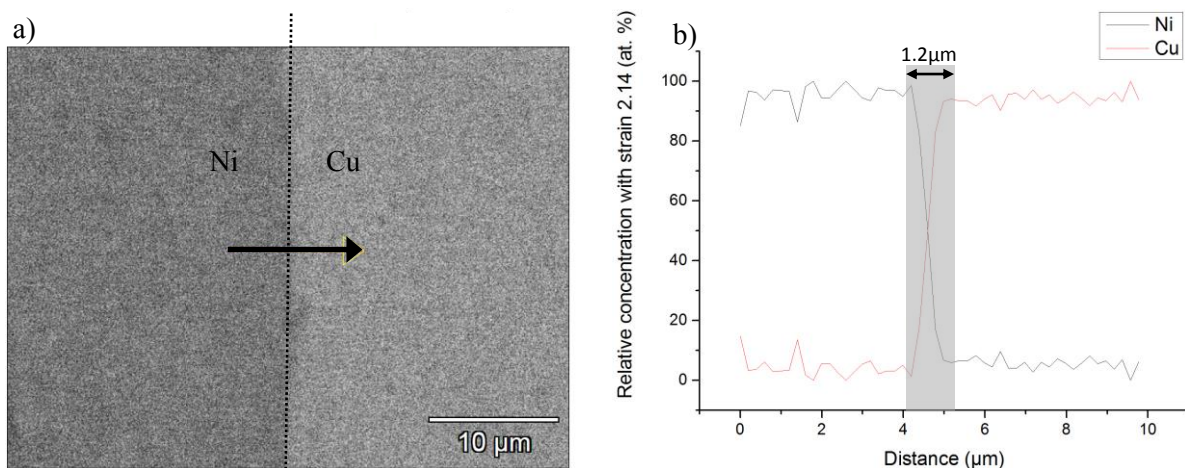


Figure 3. a) SEM image of the Ni-Cu interface region from the 1305 μ m coated sample after 8 passes of swaging ($\epsilon=2.14$) taken at 15kV. b) EDX scan over the line selected in a) showing the Ni and Cu content for each point in at.%.

The chemical analysis shows the interaction between Cu and Ni existing in an interface region which reaches a width of about 1.2 μ m. Note that the extend of Cu into the Ni phase is of the same magnitude as the extend of Ni into the Cu phase and in the order of $\sim 1\mu$ m. This correspondence has its cause in the similarity in atomic radii of both Cu and Ni and the full intermixability. Both scans show a similar sized intermixing region between the Ni and Cu. The area where both Ni and Cu is present is of the same width. There is no increase in the width from strain $\epsilon=0.47$ to $\epsilon=2.14$. We also have to be careful as the maximum spatial resolution of the EDX system is depending also on the thickness of the sample and the probesize [4] and in this case is around 1 μ m. From the data we can see that we are already close to this limit. The bonding itself, however, seems perfect and there are no crack visible even at the highest deformation.

3.2. Microstructure evolution

TEM investigations of the microstructure of the sample show the evolution of the deformation microstructure at increasing strain (see Fig.4). Cu in the as received condition is illustrated in Fig.4a, showing a very fine grained structure with single dislocations and dislocation boundaries within the

grain. The average grain area is about $889\mu\text{m}^2$, see Fig.4b, suggesting that the Cu in the as received condition is in a hot/cold deformed state. At a strain of $\epsilon=0.15$, Fig.4c and Fig.4d show evolution of a fine deformation structure containing a network of dislocation boundaries forming a loose cell structure (Fig.4c). This structure evolution does refine during a strain increase to $\epsilon=0.65$ and a well-defined cell structure has evolved. The average area of these cells is $201\mu\text{m}^2$ (Fig.4e). In the structured characterization the grain area can be surrounded by cell subgrain- and grain boundaries. In the text, grain area is used as a descriptive phenomenon.

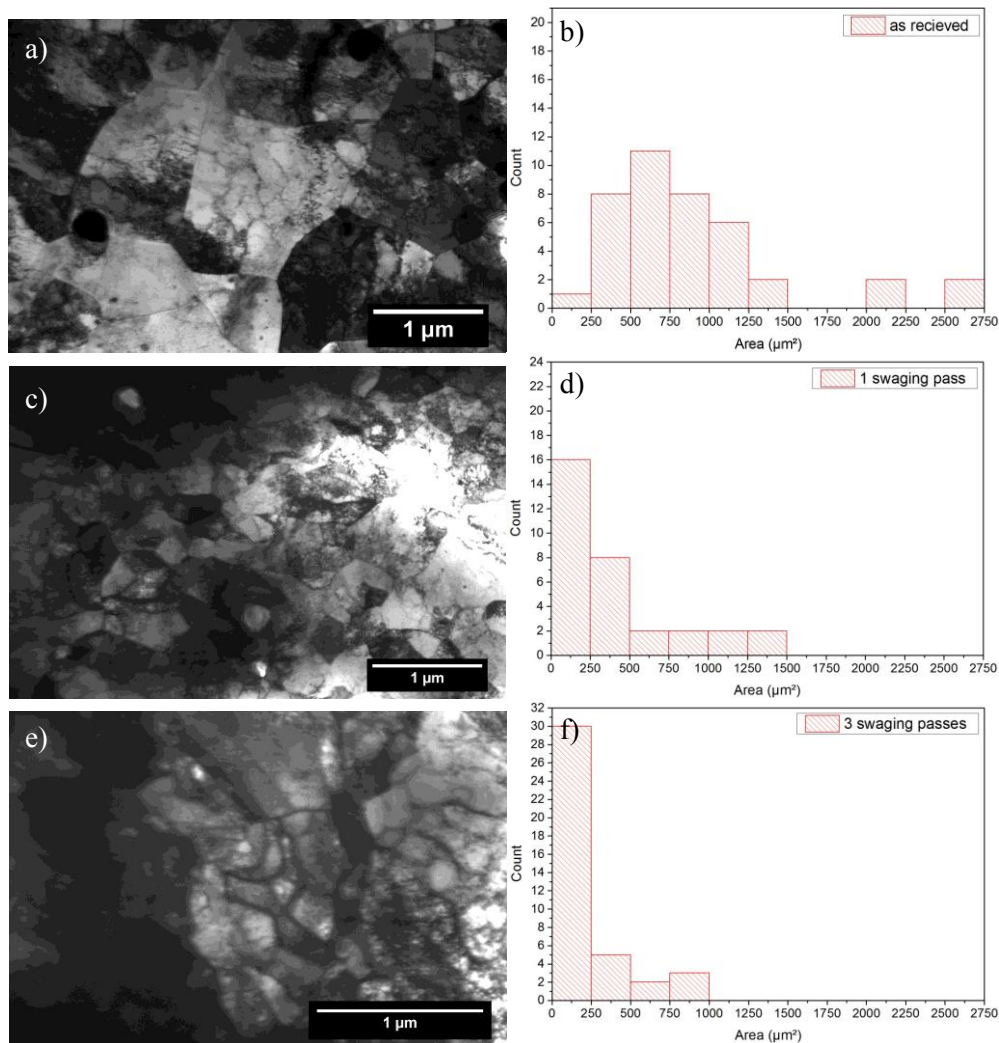


Figure 4. TEM micrographs and grain size distribution for a $50\mu\text{m}$ Ni coated Cu rod. a), b): as received sample; c), d): after 1 pass of swaging and a strain of $\epsilon=0.15$; e), f): after 3 passes of swaging and a true strain of $\epsilon=0.65$. The sample is taken from a position away from the Cu/Ni interface.

The TEM images in figure 4 a), c) and e) give a qualitative impression that with increasing strain, the structure refines. The quantitative analysis in figure 4 b), d) and f) also proves this. While for the unstrained sample the most common grain areas lay between $500\mu\text{m}^2$ and $750\mu\text{m}^2$, the dominant grain area for that strained samples lays below $250\mu\text{m}^2$, where after 3 passes of swaging and a true strain of $\epsilon=0.65$ the percentage of small grains below $250\mu\text{m}^2$ is larger than after 1 pass and a strain of $\epsilon=0.15$.

A decreasing grain area with increased strain is expected and also gives rise to an increase in hardness for the system.

3.3. Microhardness development

Microhardness indentation measurements according to the Vickers method have been conducted on the differently strained samples to correlate the microstructure evolution with the hardness development. The hardness is measured in the Cu phase in a position away from the Cu/Ni interface to allow comparison with the observed microstructure.

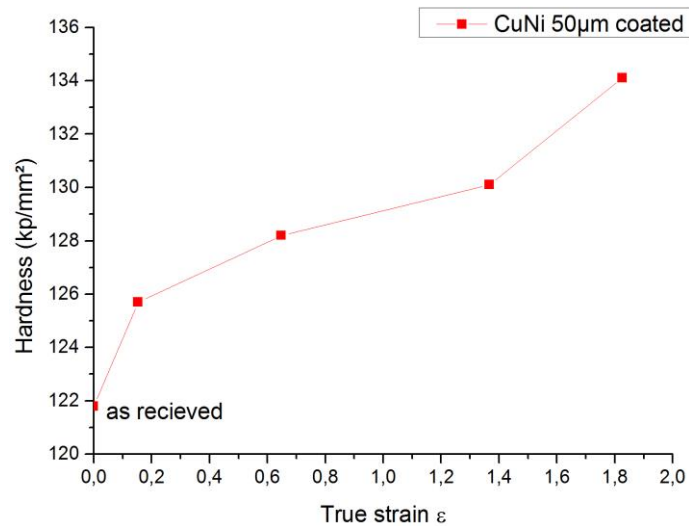


Figure 5. Microindentation hardness development of the 50µm Ni coated Cu rod when being strained up to a value of 1.83. Each point is the arithmetic mean value of 10 indentations taken from the same area in the Cu.

With increasing strain the hardness increases a limited extend from 120 to 134 kp/mm². The initial hardness indicates that the Cu rod as received is almost fully hardened in agreement with the fine microstructure shown in Fig.4a. As to the small hardening rise shown in Fig.5, it reflects typical stage IV hardening in Cu with an almost constant hardening rate.

Following the swaging deformation, the samples were annealed at 200°C for 0.5h, 1h, 2h and 4h (see Fig.6). A small hardness decrease is observed after annealing for 0.5h, which may be caused by annihilation of a small amount of dislocations. At larger annealing times the hardness increase with time suggesting that solutes in the Cu with an industrial purity (see Table A in the appendix) may segregate to the defects in the deformation structure and pin the dislocations. This segregation does apparently stabilize the deformed structure showing no sign of nucleation and recrystallization during the heat treatment.

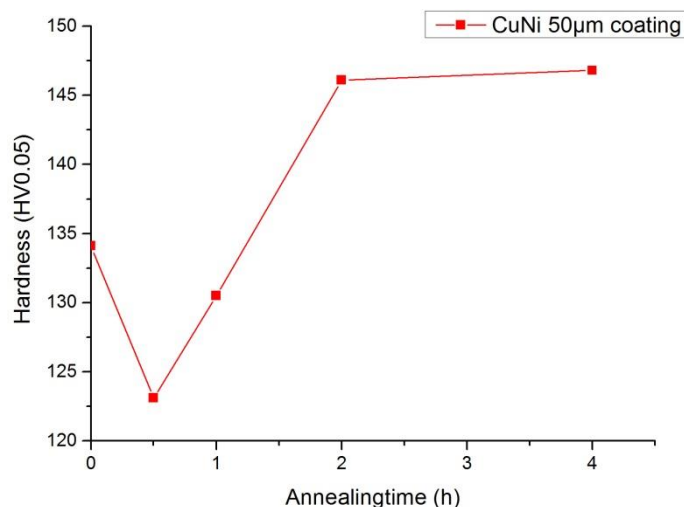


Figure 6. Microindentation hardness development for the 50µm Ni coated Cu rod after swaging and strain of 1.83 and subsequent annealing. Each point is the arithmetic mean value of 10 indentations taken from the same area in the Cu.

4. Concluding remarks

The application of rotary swaging has been successful in forming a defect free metallurgical bonding between a Ni coating and a solid Cu rod. The depth in which intermixing takes place is about 1µm creating an interface layer of about 1.2µm in thickness. By choosing the swaging process it is possible not only to produce a surface layer with improved corrosion resistance, but also to introduce a residual compressive stress in the sample, which may improve its fatigue resistance to be tested in a next step.

The intermixing interface layer is formed by mechanical alloying and it is of interest to study this layer in detail by Transmission Electron Microscopy (TEM) combined with 3D atom probe characterization. This is in order to shine light on the interaction between solute elements and the defects in the deformed microstructure in the form of dislocations, dislocation (cell) boundaries and deformations induced high angle boundaries. This interaction is important to understand fundamental processes such as dynamic and static recovery and recrystallization in metals containing a small amount of solutes, but also to optimize process and materials selection for advanced technological applications of a new approach.

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Appendix

Table A: Impurities present in the commercially pure copper rods used.

Percentage	Chemical element
99,995%	Cu
0.0003%	O
0.0012%	Ag
0.0012%	S
0.0002%	As
0.0005%	Pb
0.0005%	Sb
0.00003%	Bi
0.0001%	Se
0.00005%	Te
0.0001%	P
0.0005%	Ni
0.00005%	Zn

Table B: Content of the electrolytic solution used to coat Ni onto the Cu rod. The total volume used was 1 liter.

Weight	Percentage	Chemical formula	Scientific name
300g	78,5%	Ni(II)SO ₄ (H ₂ O) ₆	Nickelsulfate-hexahydrate
45g	11,8%	Ni(II)Cl ₂ (H ₂ O) ₆	Nickelchloride-hexahydrate
37g	9,7%	H ₃ BO ₃	Boric acid
Water was added for 1 liter liquid			

Table C: Content of the solution used to etch the Cu rods before the swaging. The total volume used was 1 liter.

Volume	Percentage	Chemical formula	Scientific name
0,5l	50%	H ₂ SO ₄	Sulfuric acid
0,2l	20%	HNO ₃	Nitric acid
0,01l	1%	HCl	Hydrochloric acid
Water was added for 1 liter liquid			