Examination of first and second order thermodynamic realignments of metals and metal-alloys, with application of DMTA equipment

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Abstract
The researcher work pushes the borders of the application of a high efficiency equipment, in the matter of metals. With this equipment, which already testified in the compound industry, a flasher query of some metal-related technological parameters could be easily available. Towards the searching, we shaped different compound copper-alloy samples, in different states, and accordingly we monitored the realignments. Following the shaping, the DMTA detected such microscopic transformations (as we expected), according to heating rate, whereby we could determine the specialities of the transformations. In order to monitor the effect of the work hardening, we applied two different shaping grade: 50% and 75%. The heat treatment already took place in the DMTA, using 3 K/min heating rate. The specimens were loaded by inflection in the 2-point bending support with constant frequency and amplitude. Our current object was the monitoring of the recrystallization, and the investigation of the influential factors of this process, but other transitions were also regarded. Those measurements’ results, that the DMTA presented, had been compared with DSC and hardness analysis, whereby we try to conclude to the utility of DMTA, in matter of metal alloys.

Keywords: DMTA, recrystallization, DSC, hardness analyze, tin-bronzes, brasses, viscoelastic

1. Introduction
The researcher team examines both the industrial metals (principally) as well as the high-tech materials and special metals (for example shape memory alloys) with DMTA equipment. Our main object is the monitoring of the recrystallization, in case of copper alloys and the investigation of the influential factors of this process. The measurements’ results, that the DMTA presented, had been compared with DSC and hardness analyses.

The literature research added up to that, we are not the first to examine metals with DMTA. But other (particularly Asian) researchers usually take into consideration the copper as alloying element or as compound, not as all-metal. For example Tang et al. examined the structure of copper electopolyurushiol film. The EPU-Cu2+ film was characterized by dynamic mechanical thermal analysis, but the Cu2+ content in the coordination polymer is only 8.63 %, as compound [5]. There are still many events, when the copper gives the base for surface treatment. Loo et al. investigated N,N-dimethylthioacetamide adsorbed on Ag and Cu electrode surfaces. The comparison was made by vibration analysis of DMTA [6].

In contrast with them, we would like to write up the measurement method, whereby the properties of the industrial material itself, would be easier defined.
The DSC detected the convection, due to energy release or energy attenuation. The DMTA is able to load mechanical stress, next to heating [1]. Therefore it can determine the changes of the mechanical properties, otherwise than DSC. Furthermore, it is a very precise instrument. The exact temperature monitoring with hardness analyses are difficult because of the variation of the furnaces’ constant temperature [2].

In case of a visco-elastic material the σ bending stress is delayed to the deformation with delta angle (figure 1). In case of clearly viscous materials, like the water, the delay is 90°. Because the copper alloys are elastic materials, the σ bending stress and the deformation should have been in the same phase [1].

![Figure 1. DMTA curve](image)

In the curves of the DMTA, the loss factor appeared. It means that in certain cases, the investigated copper alloys also can show similar properties than visco-elastic materials.

2. Method

2.1. Samples

The baseline was four different compound copper alloy ingots. The rolling was started from 15 mm thickness, on 500°C. This relatively low temperature ensured the avoidance of the oxidation. Samples were manufactured from all of the ingots on 2 mm and on 4 mm thickness. Next to four different compositions, it means eight pieces of samples. All of the samples were softened one hour.

After that, all of the samples were rolled to 1 mm thickness, on room temperature. Based on this I made two different shaping grades. In case of the initial 4 mm thickness samples, the deformation grade became 75%. In case of the initial 2 mm thickness samples, the deformation grade became 50%. It is well known, that the temperature of the recrystallization is depend on the structure, and the shaping grade of the material [4]. In this way I tried to monitor both the effect of the shaping and the composition during the searching.

I selected such copper alloys, which processing is done by forming. It was necessary because of the recrystallization. The mark of the samples originated from University of Miskolc. The determination of the exact composition was done by spectrometer:

- sample 31 (sample 10): 58.8 % Cu 40.9 % Zn
- sample 24: 61.3 % Cu 26.8 % Zn > 5 % Ni
- sample 21: 91.5 % Cu 6.19 % Sn
- sample 23: 95.8 % Cu 3.70 % Sn

At first sight, the samples can be partition into two groups:

- the first two samples are brasses: (31, 24)
- the last two samples are tin-bronzes: (21, 23)

Examining brasses, in case of the sample 24 the average Zn content is lower than 30%, and the average Ni content is more than 5%. Based on this, the sample 24 belongs to formed brasses. The sample 31 may seem rigid alloy because of the high Zn content. However, in the lack of other elements, it also can be organized to the group of formed brasses [3].
In case of the tin-bronzes, the average Sn content is between 2% and 14%, and there are no casting type elements. So these samples belong to the group of formed tin-bronzes [3].

2.2. Preparation
I applied two point bending method. The measurement frequency was 5 Hz, the amplitude of the elongation was 10 µm. The measurements were carried out in air. The DMTA provided the heating of the samples with 3 K/min heating rate. The DSC samples were manufactured by cutting. The cutting made the samples’ structure formed, therefore some DSC measurements failed. Furthermore I had to clear the samples in alcohol. The hardness analyses were done by Instron Wolpert 2100B Vickers hardness tester. The samples were heated from room temperature to 500°C. The frequency of the measures was increased between 400°C and 500°C, for more precise results. Five parallel measurements were done in all temperatures. The edge values were left and the middle three values’ average was taken.

3. Results
In case of copper alloys, the peak of the loss factor is around at 0,1 and 0,2 on the DMTA curves. The value is smaller than polymers by one decimal digit. The value of the loss factor is usually about at 1,5 at polymers.

3.1. Sample 21 (tin-bronze)

The transitions are well visible in both diagrams. The blue curve shows the 75%, the green curve shows the 50% deformed sample. The main peaks around 470°C, refer to the β-β’ transitions. The temperature of β-β’ transition is as lower as the deformation higher. It is also true for the recrystallization. The bigger deformation grade gives the bigger area under the curve. The recrystallization starts at around 400°C, according to the hardness analyze (figure 3). The smaller, tanδ peaks would refer to it (figure 2).
3.2. Sample 23 (tin-bronze)

The β-β transformations are clear in both cases. Unfortunately the recrystallization is not visible in the curves. On the left side of figure 4, a little peak can be seen roughly on 400°C, which refer to it. It is justified by the DSC curve on figure 5. The recycling is also clear, in lower temperature range, at 271°C. The curve of the 75% deformed sample (right) is flat until it reaches the β-β transformation point. The reason for this believed, that too small grains grown up during to the recrystallization, which can’t display the transition. The temperature of β-β transition is also as lower as the deformation higher again.
3.3. Sample 10 (brass)

Based on the results, I conclude that the recrystallization takes place at around 300°C, lower than tin-bronzes. It can be clearly seen in case of 75% deformed samples, but no peaks appeared on 50% shaped sample’s curve. The $\beta$-$\beta'$ transitions are also visible, as in the previous cases. The diagram clarifies well the discrepancy between the effects of the shaping grade. The biggest area under the curve, and the lower temperature of $\beta$-$\beta'$ transition belongs to the biggest deformation, which is shown by the blue curve.

![Figure 6. DMTA curves of sample 10, tanδ highlighted: 50% (green) and 75% (blue) shaped](image)

The place of the DSC peaks was changed by the heating rate. But it still can be seen, that the recrystallization happened around 300°C as the DMTA and hardness analyze (figure 8) show.

![Figure 7. DSC curve of sample 10](image)

![Figure 8. Hardness analyze result of sample 10](image)
3.4. Sample 24 (brass)

Figure 9. DMTA curve of sample 24, 75% (left) and 50% shaped

In case of 75% deformed sample, the $\beta$-$\beta'$ transition took place such high temperature, that was outside the boundaries of the measuring. There is an uncertainty at around 450°C, which is maybe not enough to declare the recrystallization, but according to the DSC (figure 10 left) and the hardness analyze (figure 10 right) it should be there. In lower temperature range, between 200°C and 250°C, the recycling appeared.

In case of the 50% deformed samples, only the $\beta$-$\beta'$ transformation can be seen. This is already the second event of brasses, when the recrystallization does not appear at lower deformation grade.

Furthermore it should be mentioned that the highest loss factor values are shown by the DMTA curve of sample 24. Both curves’ peaks transcend the 0,2 tan$\delta$ value, the more deformed sample better, the less deformed sample less. Based on this it is observed, that this sample is the most elastic.

Figure 10. DSC curve (left) and hardness analyze result (right) of sample 24

Left, on the DSC figure, the first peak refers to the recycling, the next one refers to the recrystallization. The end of the process is not in the figure, as in the case of DMTA.

4. Conclusion

Realignments of copper alloys were investigated in different circumstances. To reveal the transformations we applied DMTA, DSC equipments, and hardness analysis. Transitions have been demonstrated in several cases. $\beta$-$\beta'$ transition is always visible, expect only in one or two times. In case of brasses, the presence of the recrystallization depends on the shaping grade. It is never appeared under 75% deformation. The recycling is visible in more cases in lower temperature ranges.

Based on the results, we succeeded in demonstrating the appearance of the loss factor, with this new measurement process. Furthermore, it is observed, that the thermo-dynamic measurement process is a suitable method for monitoring realignments.
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