Effect of Copper Precipitates on the Toughness of Low Alloy Steels for Pressure Boundary Components

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Summary

The ferritic bainitic steel 15NiCuMoNb5 (WB 36) is widely used for pressure boundary components. Due to the high copper content which leads to precipitation hardening high strength and toughness are characteristic for this type of steel. However, in the initial state, there is still a high amount of dissolved copper in an oversaturated state which makes the steel susceptible to thermal ageing. Ageing and annealing experiments were performed, and the change in microstructure was investigated by small angle neutron scattering (SANS), measurements of the residual electric resistance and hardness measurements. A correlation between micro structural changes and changes in mechanical properties could be established. It could clearly be shown that significant effects on strength and toughness have to be considered when the size of the copper rich precipitates vary in the range from 1.2 to 2.2 nm in radius. The changes in microstructure affect both, the Carpy impact transition temperature and the fracture toughness qualitatively and quantitatively in a similar way. The investigations have contributed to a better understanding of precipitation hardening by copper not only for this type of steel but also for copper containing steels and weld subjected to neutron irradiation.

1 Introduction

The copper alloyed ferritic steel 15NiCuMoNb5 (WB36) is widely used for pressure boundary components in the temperature range up to 340 °C. High strength properties and at the same time high toughness are the main reasons for the application of this type of steel, Table 1. Due to the content of alloying elements (Ni and Mo) the steel forms a ferritic bainitic microstructure with a certain portion of copper precipitates in the ferrite when quenched in air, **Figure 1**, and thus, uniform properties across the wall can be achieved even for thick walled components with complex geometries.

In the past, it was recognised that thermal ageing occurs during service which leads to an increase in ultimate strength and to a significant reduction in toughness in terms of an increase in the ductile/brittle transition temperature, **Figure 2**. The basic mechanism for that is a change in the precipitation state of copper. According to the specification, the steel contains 0.45 – 0.85 % copper which is only partly precipitated at room temperature after manufacturing. About half of the amount of copper is still dissolved in the lattice in an oversaturated form because the equilibrium state is usually not reached during the heat treatment process and copper is almost not dissolvable in steel at room temperature, **Figure 3**. At service temperature a precipitation hardening process occurs, leading to fine disperse precipitation of copper. The amount and the particle size of the copper precipitates depend strongly on temperature and time and determine the change in strength and toughness properties during service. The aim of the project was to study the process of precipitation hardening and to establish a correlation between the precipitation state and the mechanical properties.

2 Investigations

The precipitation behaviour was investigated in long range thermal ageing tests up to 19000 h, predominately at 400 °C. The change in microstructure was evaluated indirectly on the basis of hardness measurements and measurements of the residual electric resistance (G value). This method utilises the effect that the electric resistance decreases with the decrease in the number of dissolved foreign atoms. As a direct measure of the precipitation state, small angle neutron scattering (SANS) measurements were performed. This leads directly to quantitative information about the mean particle radius (a) and the corresponding volume fraction of copper rich particles (b) for the given size distribution, **Figure 4**. Based on the assumption of spherical particles the total amount of precipitated copper can be determined.

Several material states were investigated, the results of which will be presented in this paper to outline the present perception about the precipitation processes in the material. The investigated material states were:

* initial state (as delivered)

* component after service (boiler drum) operated at 350 °C for 57000 h
* thermally aged at temperatures from 350 to 500 °C
* stabilising heat treated
* recovery annealed after service
* material after low cycle fatigue loading (temperature and plastic deformation)

To evaluate the relevance of the ageing process with regard to the life assessment of a component the change in the microstructure was correlated with the change in Charpy impact energy and fracture toughness.

In order to separate the effect of copper precipitation from other effects which might be caused by thermal ageing, a low copper high strength fine grained steel 22NiMoCr3-7 (0.10 % Cu) was included in the investigation for comparison purposes.

3 Results

During the hold time at tempering temperature of 600 – 650 °C, the largest portion of copper is in solution. In the cool-down phase of the normal heat treatment of the manufacturing process, only part of the total amount of copper is being precipitated. However, since in the first stage of cooling the precipitation occurs at high temperatures, and some time is available, the particles can grow leading to the specified strength and toughness of the steel. With decreasing temperature less growth occurs, which can be derived from the Arrhenius equation, and at temperatures below 300 °C, no relevant precipitation occurs anymore.

The thermal ageing experiments showed clearly that the micro structural changes can be detected by the change in the residual electric resistance (G value) and the hardness. The G value increases up to a point where all copper is precipitated and then stays at a constant level, **Figure 5**, whereas the hardness reaches a maximum before all copper is precipitated. After the maximum, the hardness decreases with time due to a growth of the particles although additional small particles are still being precipitated , **Figure 6**. The G value and the hardness of the low copper steel as a function of time is also shown in Figure 5 and 6, respectively. The stable behaviour confirms that no relevant precipitation occurs in this steel and that the changes observed in the steel WB36 have to be attributed to the process of copper precipitation.

The typical precipitation pattern of the quenched and tempered state is usually of a bimodal form, see Figure 4, with only very little amount of copper (0.003 %) precipitated with a mean radius of 0.85 nm and a larger amount of copper (0.402 %) with a particle radius of 2.21 nm, **Figure 7**.

When the material is exposed to low temperature, e.g. 400 °C, small particles are being precipitated, predominantly with a radius of about 2.00 nm, see Figure 7. If the temperature at which ageing occurs is further decreased (350 °C), the precipitated copper particles are even smaller with a mean radius of about 1.27 nm.

The effect of " over-ageing" can be concluded from the comparison of the precipitation state of the material after service (350 °C/57000 h) and the one from laboratory ageing (350 °C/15000 h), see Figure 7. There are two overlapping processes that determine the hardness. During service, a higher amount of copper is precipitated (0.765 %) than during laboratory ageing (0.651 %) which causes an increase in hardness, while at the same time, the particle size increases during service contributing to a decrease in hardness. As a result of these contrary processes in this specific case, both material states show almost the same hardness, although the mean particle radius is different. When comparing the precipitated amount of copper after service (0.765 %) with the total amount of copper in the steel (0.63 %) as determined by SANS, it becomes obvious that there is a discrepancy. The reason for that is to be seen in the fact that the particles are not pure copper but copper rich particles and thus the SANS evaluation leads to higher numbers for the volume fraction.

The different kind of investigations – i.e. investigations with two independent methods to determine the amount of precipitated copper by SANS and the determination of the change in the residual electric resistance – give a clear insight into the acting mechanisms. The results from both measurements correspond well and give information about the amount of copper additionally precipitated during the ageing process, **Figure 8**.

The effect of copper precipitation can clearly be demonstrated on the basis of the Russel and Brown diagram which shows the correlation between the strength of the material and the size and amount of copper precipitates. From the theoretically derived curves for a given particle size it becomes evident that significant effects have to be considered in the range from 1 to 3 nm where the curves are relatively steep, **Figure 9**. Low temperature thermal ageing leads to precipitation of predominantly small particles in addition to the ones already present in the initial state and no significant growth occurs. This specific particle distribution leads to an increase in strength. From this diagram it can also be derived that materials can be made resistant against thermal ageing by a particular heat treatment. The aim is to precipitate as much copper as possible. If the strength of the material shall be unchanged at the specified level – assumed still to result in high toughness – the particles must have the chance to grow during the heat treatment process. This can be facilitated by extremely low cooling rate, e.g. step cooling in form of a stabilisation heat treatment over a time period of several hundred hours, **Figure 10**. Results from tensile and Charpy tests with material treated in the above mentioned way show that the specified strength and toughness values can be reached, **Figure 11**. First results of ongoing thermal ageing tests at 400 °C confirm indeed that the mechanical properties (hardness) remain stable as anticipated and thus confirm the perceptions about the micro structural mechanisms.

Additionally, ageing experiments performed at different temperatures confirm in geenral the ageing process as a function of temperature and time. Increasing temperature reduces the increase in hardness, and at 500 °C no change in hardness occurs at all, **Figure 12**, although an additional amount of copper is being precipitated as can be seen from the increase of the G value, **Figure 13**. Further investigations showed that the ageing process is reversible, i.e. a recovery annealing (620 °C/2 h) after ageing in service restored the initial lower strength and high toughness and moreover the thermal ageing behaviour was comparable to that of the initial material in the state as delivered.

To study the effect of a combination of temperature (e.g. at 350 °C) and plastic deformation (up to about 1.3 %), some low cycle fatigue (LCF) tests were performed with material aged during service and recovery annealed after service. The change in material properties after the LCF test was determined by hardness measurements. The evaluation of the LCF test results showed that both, the initial and the aged material state, have the same behaviour regarding the initiation of cracks. However, it became obvious that the hardness increase occurs much faster than under plain thermal ageing conditions even if thermal ageing is performed at a higher temperature of 400 °C, **Figure 14**. This points to the fact that the precipitation of copper is accelerated in LCF tests due to the movement of dislocations which is beneficial for the diffusion process of copper. Tests are under way to study these effects in more detail in particular to investigate the effect of the combined loading of temperature and plastic deformation on the Charpy impact behaviour. In this project, Charpy specimens will be tested which are machined from tensile specimens that were subjected to LCF loading and the test being interrupted before crack initiation, **Figure 15**. This is a necessary step to generate data which are relevant for the life assessment of a component rather than to characterise the material only on the basis of hardness data.

In order to show the link between micro structural effects and the mechanical behaviour besides Charpy impact tests, fracture toughness tests were performed and evaluated according to ASTM E 1921 with three material states which show significant differences in Charpy transition temperature:

* heat E2 after stabilising heat treatment
* heat E59 after service (350 °C/57000 h)
* heat E59 after recovery annealing of material from service

The few fracture toughness data do not only show the same tendency of ranking as in the Charpy test, the shift in temperature relative to the stabilised material state is almost of the same quantity, **Figure 16**. This shows that the conventional Charpy test is an sensitive measure to describe changes in the microstructure caused by fine dispersed copper precipitates and the results are in adequate correlation with fracture toughness data.

4 Conclusion

Investigations of components made of the copper alloyed steel WB 36 have often revealed low ductile/brittle transition temperature after service. Consequent ageing experiments and investigations of the microstructure by small angle neutron scattering have shown that an ageing process occurs caused by the change in the amount and size distribution of copper precipitates (precipitation hardening). Significant effects occur when the mean size (radius) of the particles changes in the range from 1 to 3 nm. Low temperature ageing (350 °C) leads to small particles of about 1.27 nm which may grow with increase in ageing time. Ageing at elevated temperature, e.g. 400 °C leads to bigger particle sizes of about 2.00 nm. Stabilising heat treatment (low cooling rate) has led to almost complete precipitation of the previously dissolved copper with a mean particle size of 2.29 nm. This material state is not susceptible to ageing anymore.

The ageing process can easily be detected by hardness testing. In a first phase, the hardness increases because the particles are small. In a second phase precipitation may still go on but particles tend to grow which causes the hardness to decrease after a maximum was reached. The aged material state can be restored by recovery annealing at 620 °C/2 h which leads to a dissolution of most of the particles.

The Charpy impact test reacts sensitive to this type of micro structural changes and gives adequate information about the tendency and quantity of the change in fracture toughness. A more detailed correlation between microstructure on the one hand and strength and toughness properties on the other hand still need to be established. A follow-up project is under way.

Similarities in the mechanism of precipitation hardening due to copper precipitates exist to neutron irradiation behaviour of steels with enhanced copper content where the particles are still smaller than in the aged WB 36. However, the recovery annealing of irradiated material at 450 °C causes a growth of the precipitates, whereas the recovery annealing of WB 36 at 620 °C leads to a dissolution of copper.

It was observed that thermal ageing with coincident plastic deformation accelerates the ageing process due to enhanced diffusion of copper. This effect and the consequences on Charpy impact energy rather than only on the hardness will also be investigated in detail in the follow-up project.

Acknowledement

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Table 1: Chemical composition and mechanical Properties of the steel 15NiCuMoNb5

Chemical Composition, Heat E 60							
C	Mn	P	S	Cr	Mo	Ni	Cu
0.15	1.00	0.007	0.014	0.23	0.38	1.30	0.63

$R_{p0.2}$ [MPa]	R_m [MPa]	A [%]	Z [%]	T_{41} [°C]	USE [J]
543	627	25	65	- 27	85

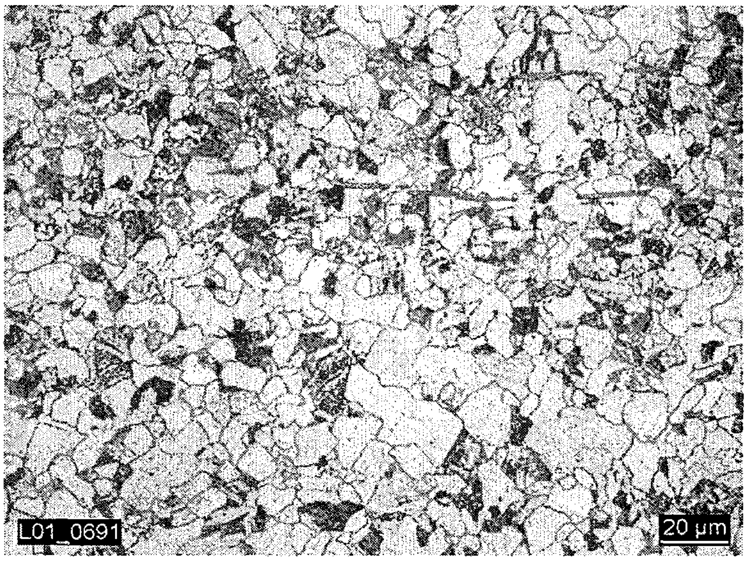

Figure 1: Characteristic bainitic ferritic microstructure of WB 36, as delivered

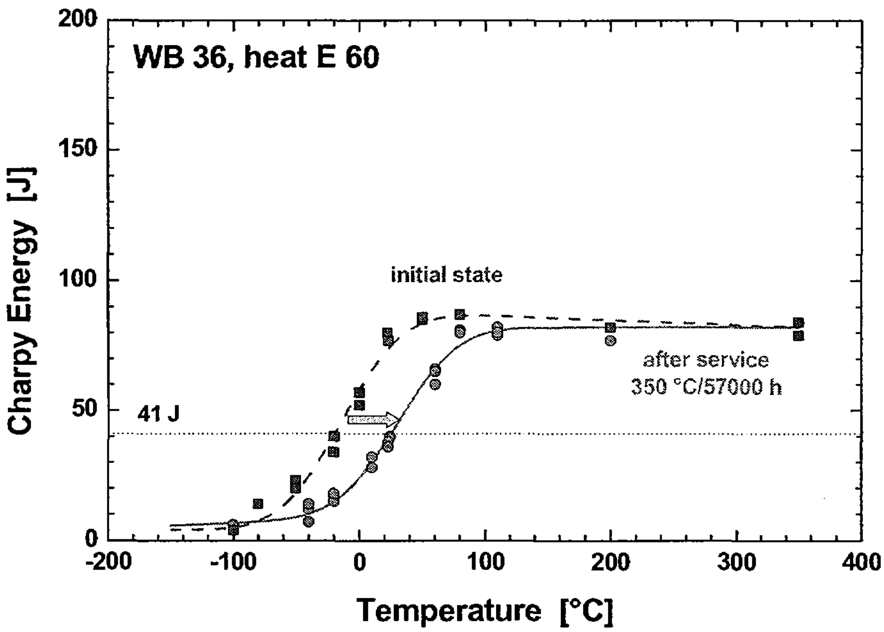

Figure 2: Charpy impact properties of the initial state and after service

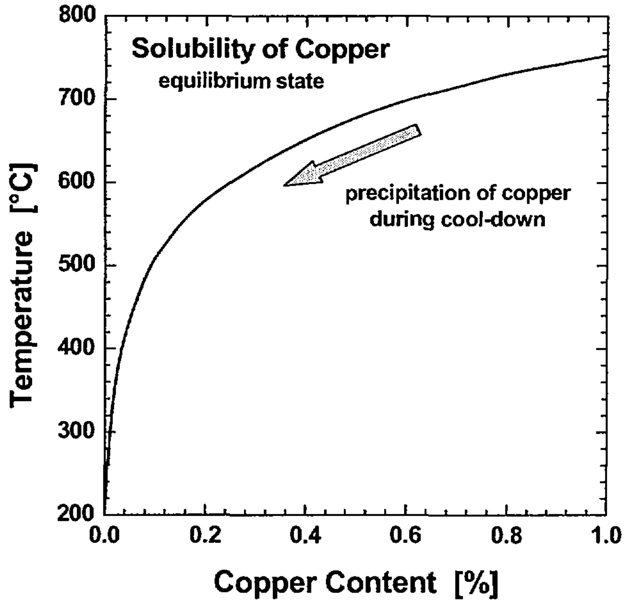

Figure 3: Solubility of copper in steel WB 36 in the equilibrium state as a function of temperature

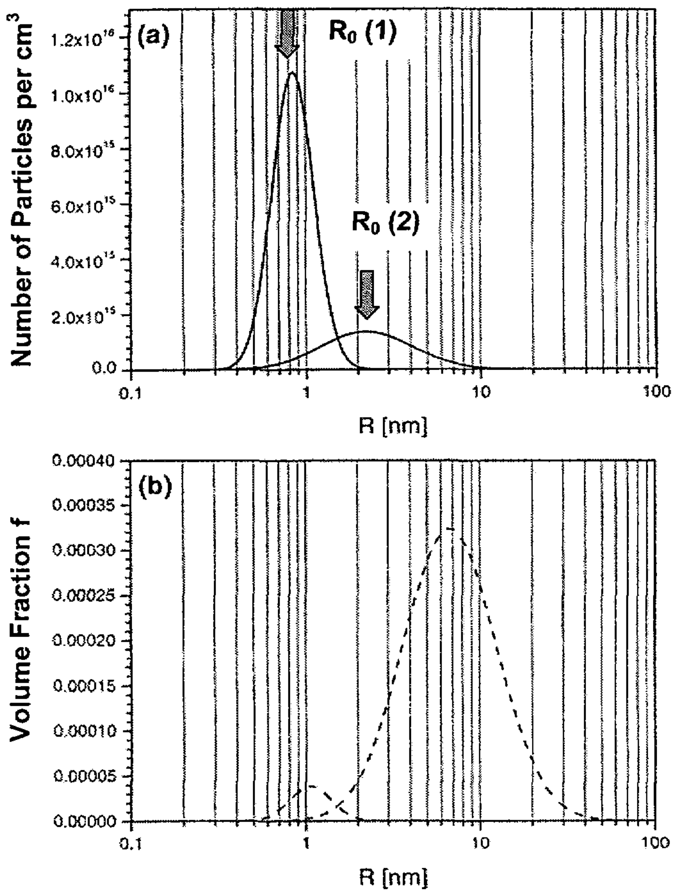

Figure 4: Number of copper rich particles (a) and resulting volume fraction (b) as determined by SANS measurements

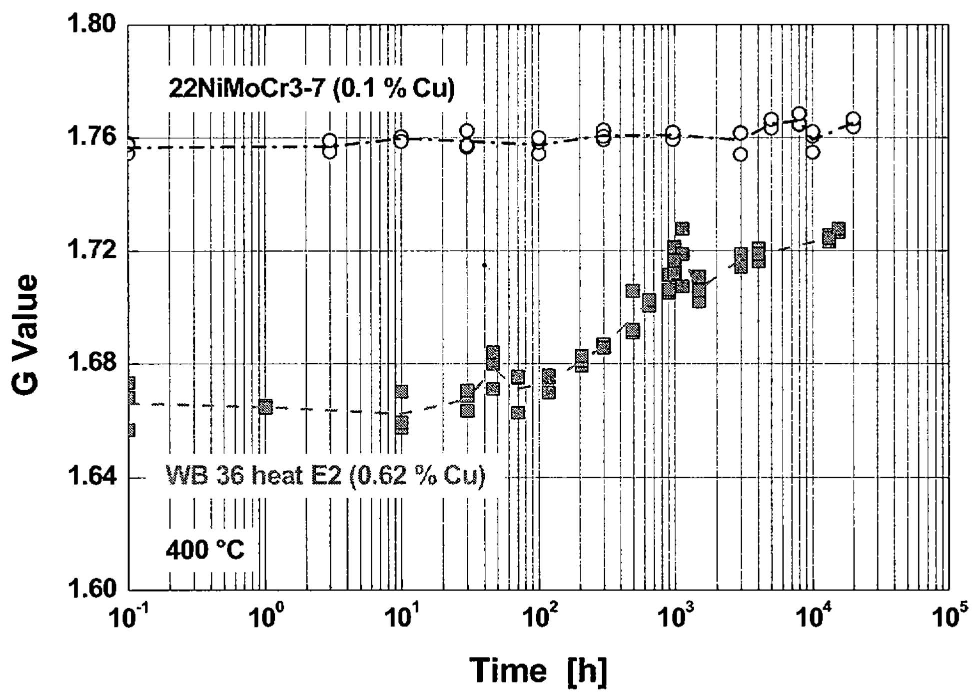

Figure 5: Change in residual electric resistance (G value) as a function of ageing time at 400 °C for a heat of WB 36 and a low copper steel 22NiMoCr3-7

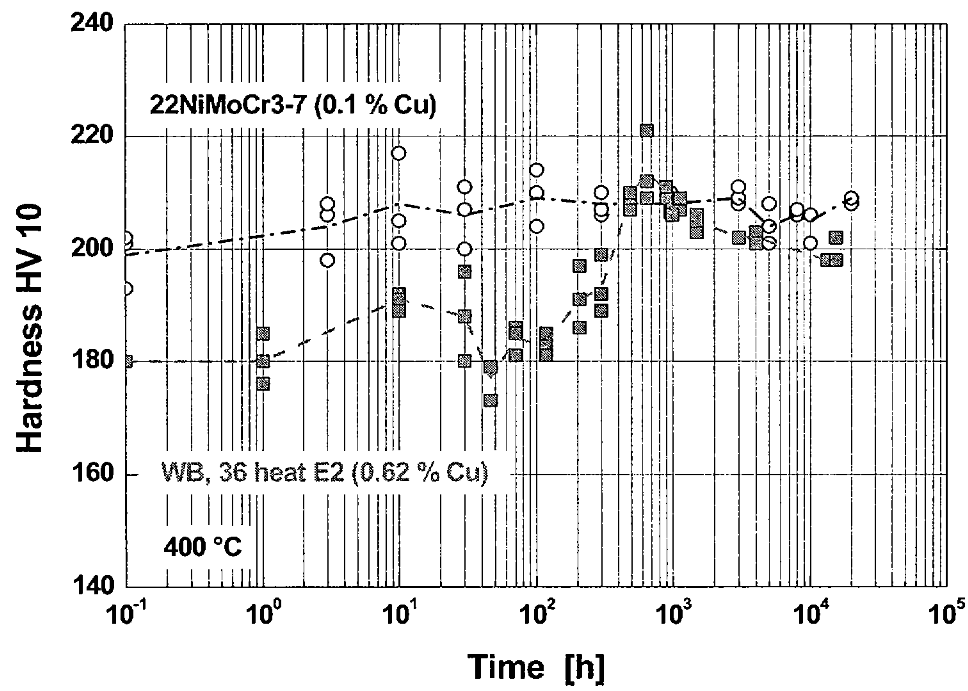

Figure 6: Change in hardness as a function of ageing time at 400 °C for a heat of WB 36 and a low copper steel 22NiMoCr3-7

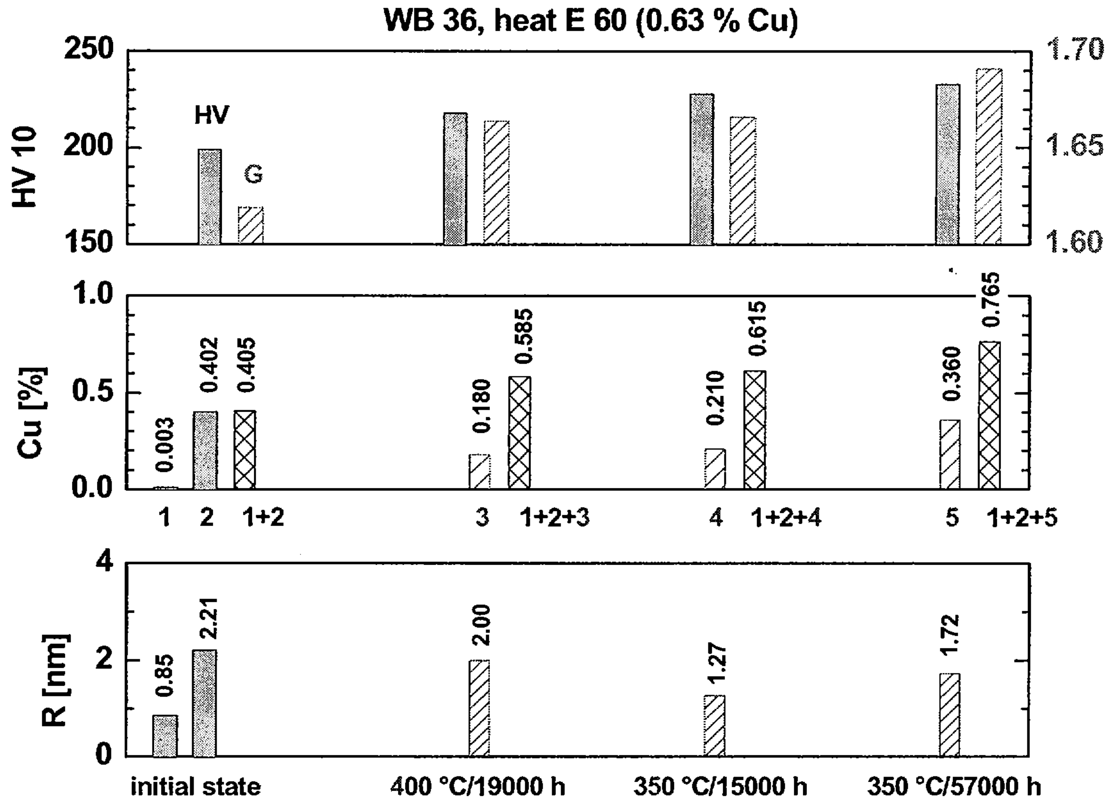

Figure 7: Change in micro structural parameters and integral properties (hardness and residual electric resistance, G value) in the initial state and after thermal ageing in laboratory tests and in service

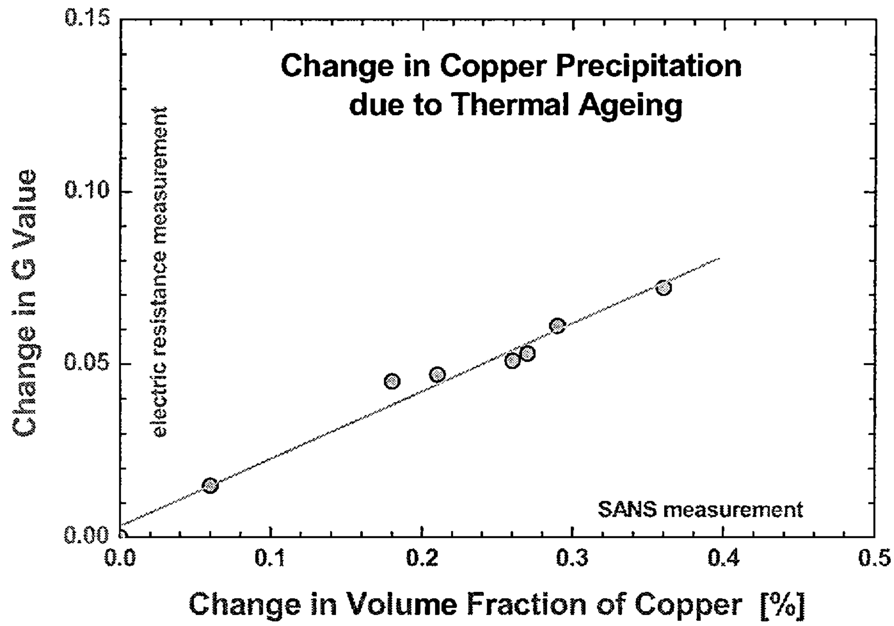

Figure 8: Correlation between Change in G value and the volume fraction of additionally precipitated copper rich particles during thermal ageing

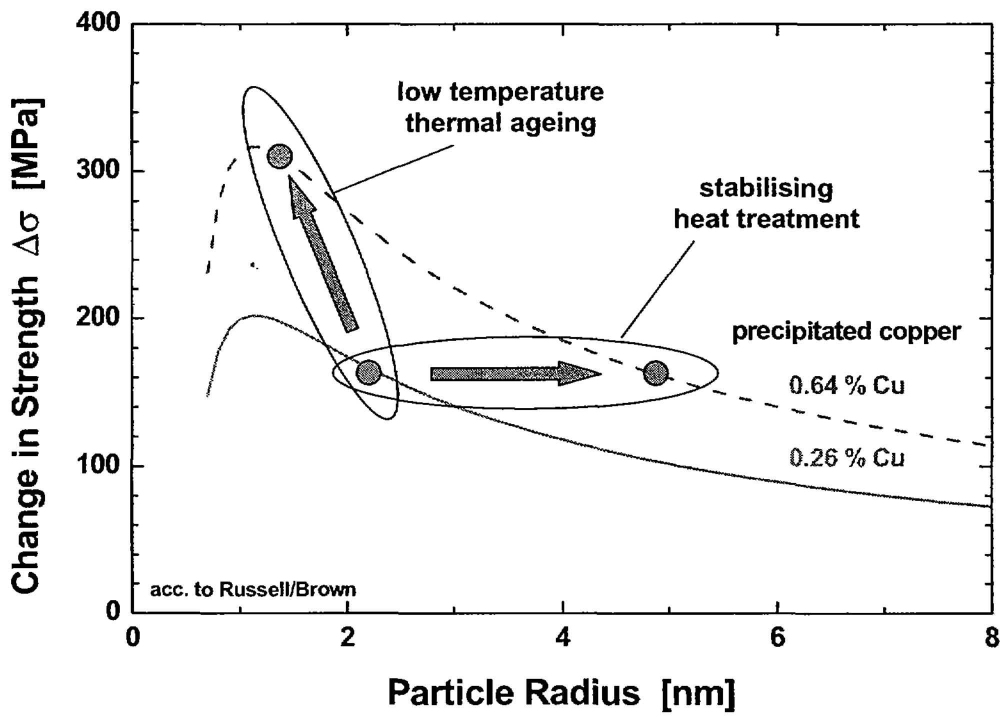

Figure 9: Change in microstructure and consequences for the change in material strength due to thermal ageing and stabilising heat treatment, respectively

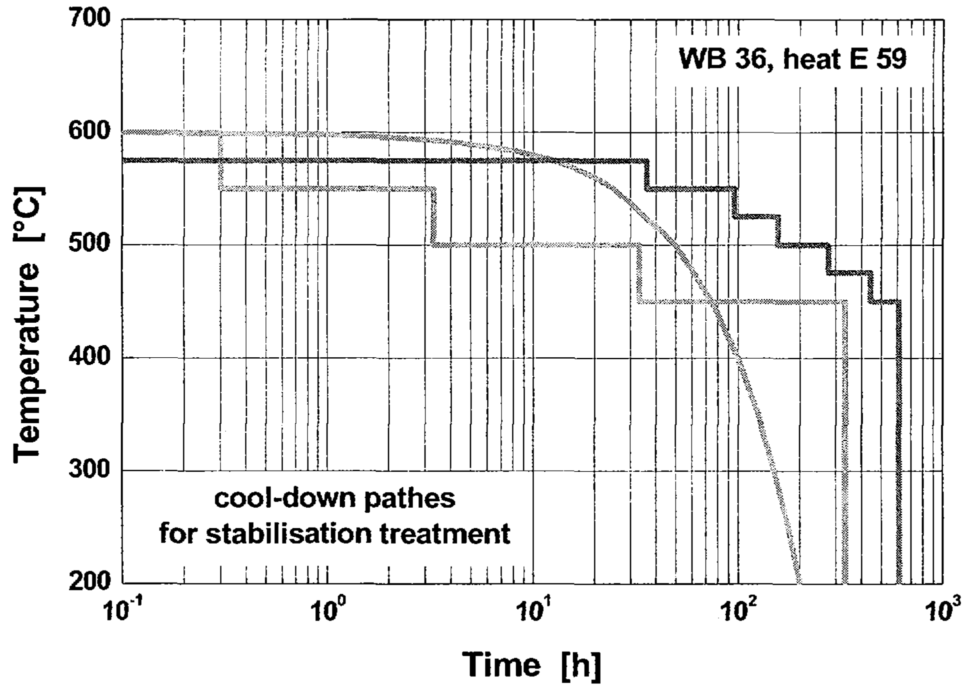

Figure 10: Possible cool-down paths of stabilisation treatments to pre-precipitate high amount of copper in form of "large" particles

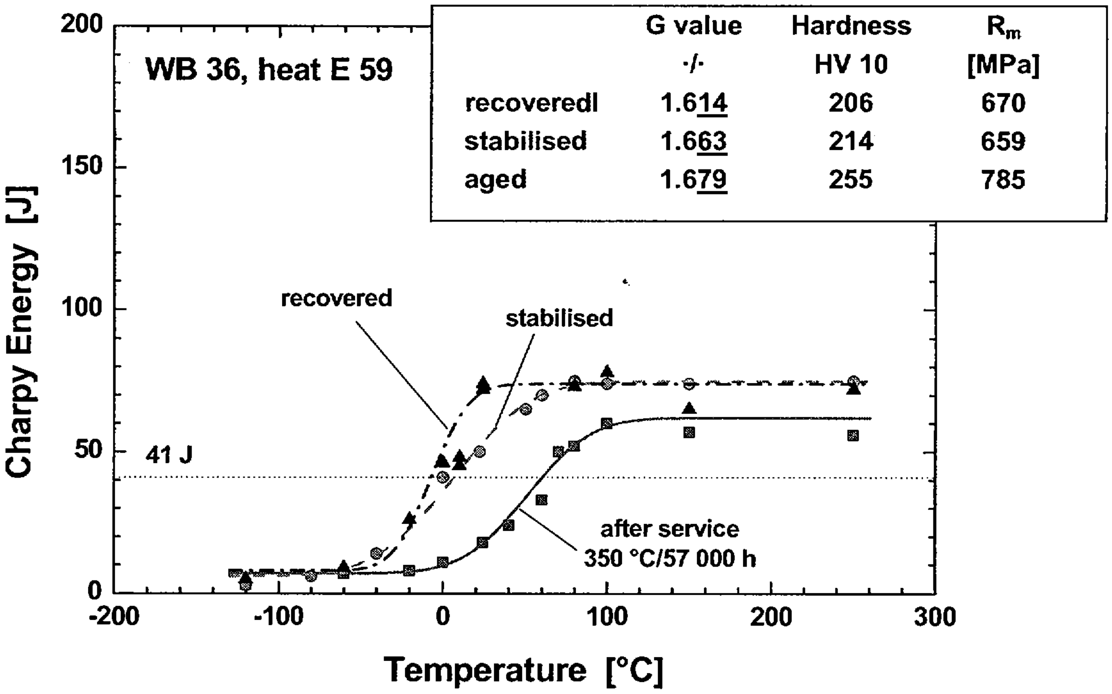

Figure 11: Strength and toughness properties of differently treated material in particular with the aim to pre-precipitate the highest possible amount of copper

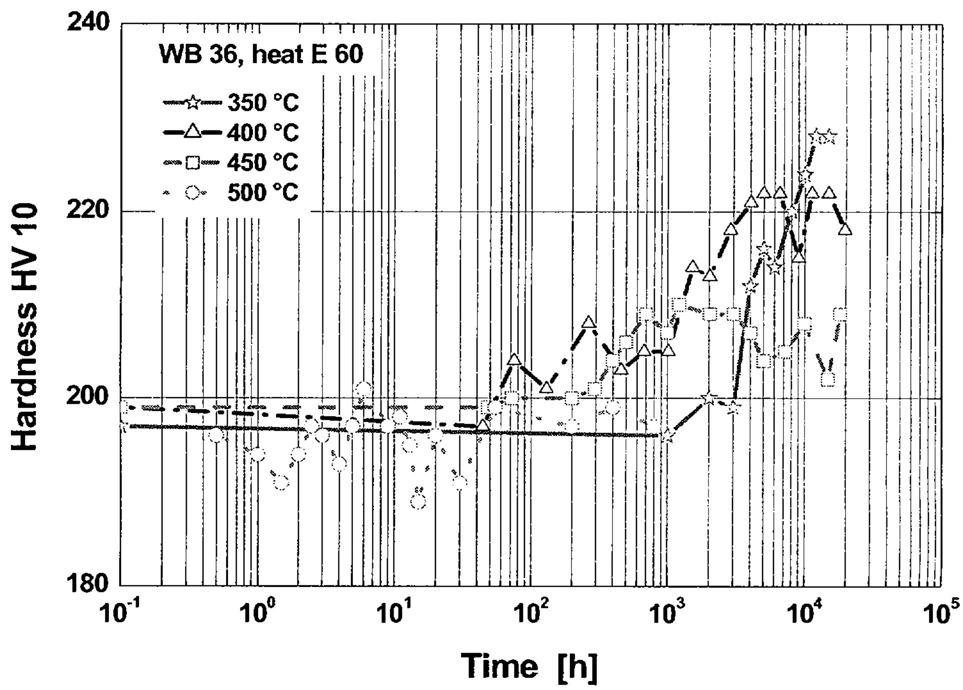

Figure 12: Increase in hardness due to ageing at different temperatures

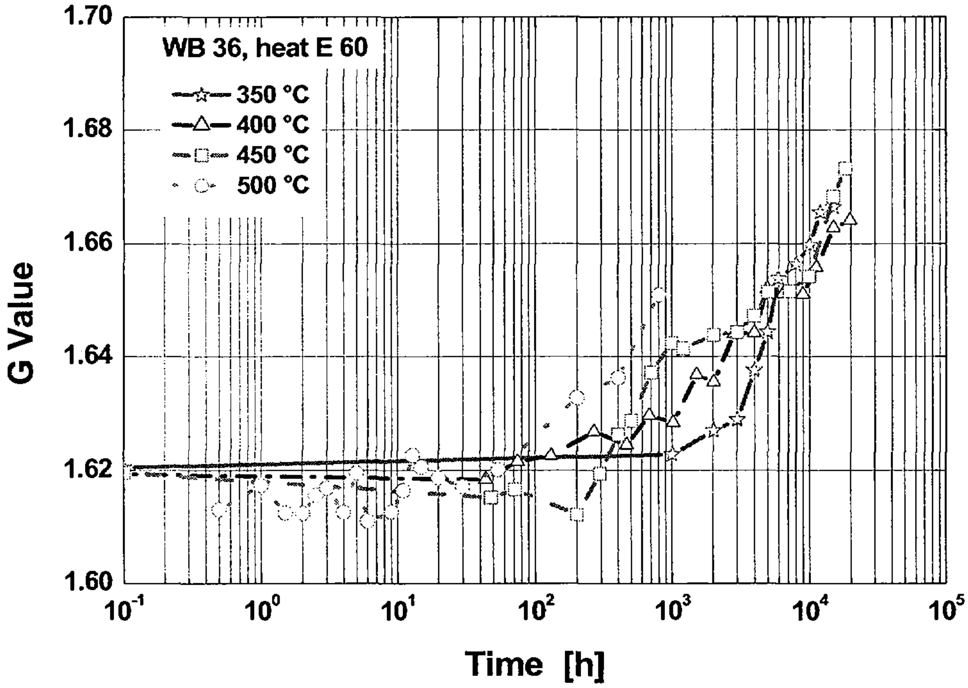

Figure 13: Copper precipitation, indicated by the increase in G value, due to ageing at different temperatures

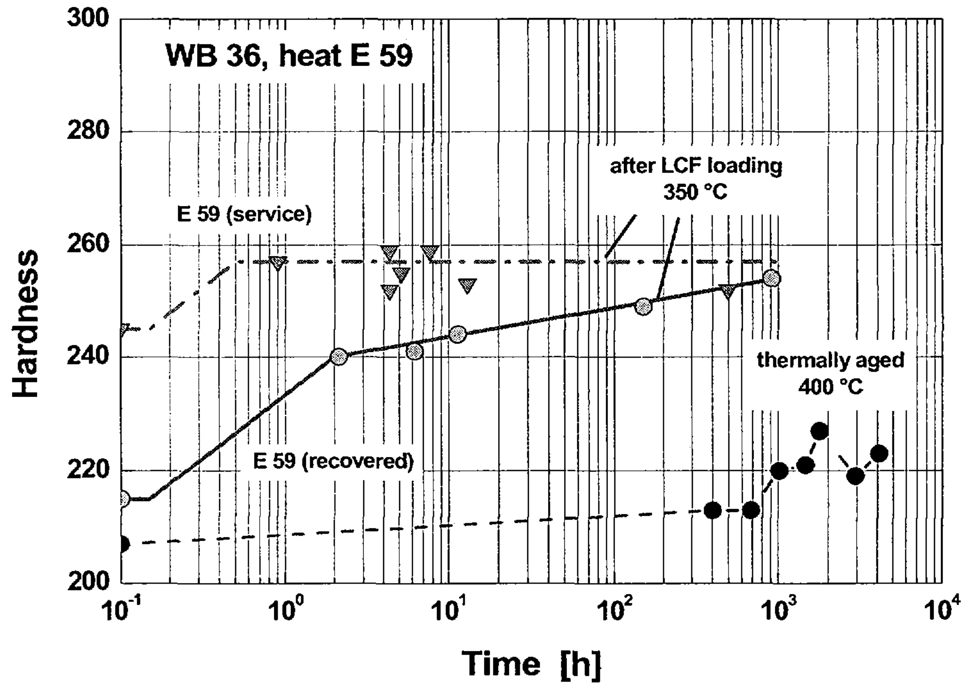

Figure 14: Increase in hardness due to thermal ageing at 400 °C and LCF loading at 350 °C, respectively

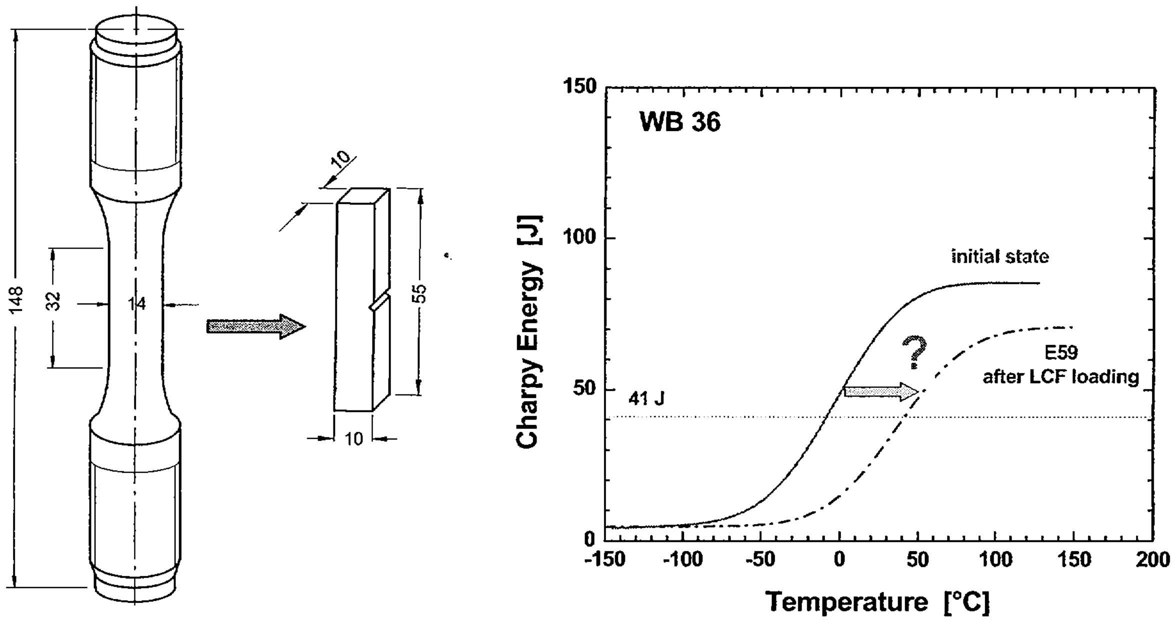

Figure 15: Ongoing project to investigate the effect of low temperature LCF loading on the change in toughness

ΔT_{41}*	E $59_{recovered}$	38 K	ΔT_0*	E $59_{recovered}$	21 K
	E $59_{service}$	87 K		E $59_{service}$	84 K

* relative to stabilised treated state

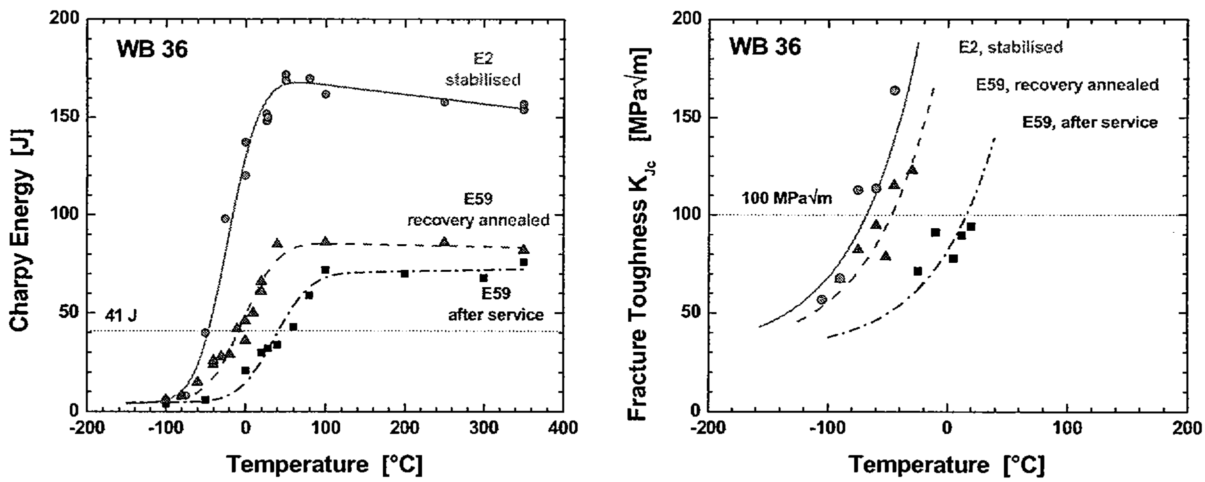

Figure 16: Correlation between Charpy impact data and fracture toughness (acc. to ASTM E 1921) of WB 36 material states with different microstructure