Hardening by annealing: insights from different alloys

O Renk\textsuperscript{1}, A Hohenwarter\textsuperscript{2}, B Schuh\textsuperscript{2}, J H Li\textsuperscript{3} and R Pippan\textsuperscript{1}

\textsuperscript{1}Erich-Schmid-Institute of Materials Science, Jahnstraße 12, 8700 Leoben, Austria
\textsuperscript{2}Department of Materials Physics, Montanuniversität Leoben, Jahnstraße 12, 8700 Leoben, Austria
\textsuperscript{3}Institute of Casting Research, Montanuniversität Leoben, Franz-Josef-Straße 18, 8700 Leoben, Austria

Email: oliver.renk@oeaw.ac.at

Abstract. In contrast to the general notion about the annealing behavior of coarse grained materials, hardening phenomena in nanocrystalline materials can occur. Although the phenomena have already been recognized several years ago, the mechanisms behind are still controversially discussed. For example, the influence of solutes segregated to grain boundaries on the strengthening mechanism is unclear. We present a combination of atom probe tomography and mechanical data to reveal the role of segregations to the strengthening. The results show that despite large modifications of the boundary chemistry the mechanical behavior remains widely unaffected. Additionally, it will be shown that hardening upon annealing can only occur below a material-specific grain size threshold value.

1. Introduction

It is well known that cold worked coarse grained materials (where precipitation hardening does not occur) undergo softening during annealing due to recovery and recrystallization. Interestingly, nanocrystalline (nc) materials can show a different behavior - hardening upon annealing instead of a softening. Such phenomena occur at temperatures where significant grain growth of the nc structure can be impeded \cite{1-2}. Although this behavior has been frequently observed, different hypothesis about the mechanisms and the origin of the hardening have been reported, see for example \cite{1-4}. While the first reports, focusing on very pure metals, attributed the observed strengthening to a reduction in the defect densities during annealing \cite{1-2}, the role of impurities or segregated solute in alloyed systems remained unclear or was expected to cause the hardening \cite{2-4}.

Since with decreasing grain size intergranular dislocation sources are thought to become dominant over intragranular sources \cite{5}, segregated solute might suppress dislocation emission from the boundaries \cite{4}. Furthermore, as in nc materials dislocations are emitted from the boundary regions and may relax immediately at the opposite boundary, also the relaxation process could be affected by the presence of segregated solute, leading to a different mechanical response.

Nowadays nc and ultrafine-grained materials (UFG) are frequently processed by methods of Severe Plastic Deformation (SPD). After the heavy deformation processes, lattice dislocations will not be completely absorbed at the boundaries and are often stored in the form of dipoles \cite{2}. These dislocations, present in the material before the heat treatment, require lower stress levels for plastic deformation when compared to the activation energy of grain boundary sources \cite{1-2}. During annealing treatments such segments or dipoles from the interior can be fully absorbed in the boundary leaving a crystal with a low
content of mobile defects behind. Additionally, the structure of high angle grain boundaries (HAGB) will change, making the emission of dislocations more complicated, which was also shown in MD simulations [6]. Also the structure of LAGB, mostly present as so called interconnecting boundaries in severely deformed metals will change, and their movement or extraction of dislocations from the boundary will become more complicated [7]. All these processes should lead to increased stress levels to activate dislocation sources after a heat treatment and to the observed hardening. Both, the annihilation of lattice defects and the segregation of impurities or solute will take place simultaneously thus, a separation of their contribution to the hardening seems challenging. Nevertheless, the role of segregations to the strengthening should be investigated further. If they play a key role, an identification of the most effective alloying elements and the interplay between them might lead to the development of ultrastrong materials.

In this study we present a combination of mechanical data of a nc austenitic steel with insights into its boundary chemistry gained by atom probe tomography (APT). These results should lead to a deeper understanding of the role of segregation to the nc-related hardening mechanism. Furthermore, as hardening upon annealing is not observed in all ufg/nc materials, additional suitable experiments were carried out to gain further insights as to why certain materials do not show the mentioned phenomena.

2. Hardening by annealing – is segregation necessary?

The idea to answer the raised question was to compare mechanical data of nc samples with similar grain size but different levels of grain boundary segregation. To do so, we used a standard 316L austenitic stainless steel. Nc structures were obtained by high pressure torsion (HPT) processing. Further experimental details can be found in Ref. [8]. The as HPT deformed structures consist of crystallites with a size of about 50 nm as calculated from several TEM micrographs by the line interception method. The corresponding microhardness was found to be 5 GPa. An isochronal annealing treatments for 30 minutes in a temperature range up to 973 K showed pronounced hardening up to 6.1 GPa at a temperature of 823 K. Measured room temperature hardness values as a function of the annealing time for the isochronally annealed samples (30 minutes) are shown in Fig. 1a). For comparison the hardness of heavily cold rolled samples is also shown in Fig. 1a. To check the thermal stability of the material and to see how fast the hardening process takes place, isothermal treatments were carried out at 823 K, the temperature at which the maximum hardness was obtained. The results are summarized in Fig. 1b). The strengthening occurs very rapidly, within 5 minutes the peak hardness values are almost reached. For longer annealing times the hardness only changed slightly before levelling off in a plateau even for long annealing times. Selected area diffraction patterns (SAED) do not reveal any additional Debye Scherrer rings of other phases formed during annealing. As can be expected from the hardness measurements in Fig. 1b significant grain growth did not occur over the wide range of annealing times. Selected bright field images of the as deformed and the annealed conditions are shown in Fig. 2. Since grain size and hardness (see Fig. 1) have not drastically changed but the amount or type of segregated solute might change over time, isothermally annealed samples could be suitable to clarify if segregation contributes to the strengthening. Therefore selected samples were analyzed by APT. A combination of APT data and the mechanical response of the samples should allow one to comment on the contribution of segregated solute to the strengthening. In the following, the major results of the study are summarized, further details of the experiments are outlined in Ref. [8].
Figure 1. Room temperature microhardness of a) isochronally annealed samples; b) isothermally annealed nc 316L samples [8].

Figure 2. TEM micrographs of a) as HPT deformed b) 30 minutes/823 K annealed c) 325 h/823 K annealed samples. No significant grain growth was observed during annealing.

Three different sample conditions were investigated by APT, the as HPT deformed samples, samples annealed for 90 minutes and 325 h at 823 K (see also Fig. 1b). APT results of these three samples are summarized in Fig. 3. It can be seen that even in the case of the as HPT deformed sample a slight average Si excess at the grain boundaries of $\Gamma = 0.15 \text{ atoms nm}^{-2}$ can be found. Short time annealing of 90 minutes at 823 K leads to an increase of the average Si excess to $\Gamma = 0.40 \text{ atoms nm}^{-2}$. Apart from the Si, only traces of other alloying elements were found for both samples, the as deformed as well as the 90 minutes annealed sample. For the long term annealed sample (325 h) boundary chemistry has drastically changed. Additionally to a similar Si excess of $\Gamma = 0.36 \text{ atoms nm}^{-2}$ than in the 90 minutes annealed samples, second phase particles could be identified at the grain boundaries. These particles contain mainly Si, Mo and Cr as can be seen in the proxigram in Fig 3. Although the temperature range where these particles have formed would suggest sigma phase formation, the average composition of the particles is far from those reported for 316L steels [9]. Further identification of the second phase was not possible from SAED patterns, which only showed reflections that would be referred to a fcc structure.
Figure 3. Results of the samples investigated by APT. a) The average Si excess of several boundaries is displayed for the analyzed samples. b) - d) Reconstruction of the APT tips with Si atoms colored in grey (b and c) and Mo atoms in red (d). d) For the 325 h annealed samples additional particles formed at the grain boundary. e) Their average composition can be seen in the plot [8].

Between annealing times of 90 minutes and 325 h in addition to the segregated Si, Mo and Cr segregate and form particles. Despite this large variation of the boundary chemistry, the mechanical properties remain widely unchanged (see Fig. 1b). From that it can be concluded that second phase particles at the grain boundary do not influence the strength of a nc material. Furthermore large variations of the type of the segregated element seems also not to have a strong effect on the strength of the material. However, possible effects of small excess values still remain unclear because during the first 90 minutes, both, the hardness but also the Si excess increased. For further clarification samples either annealed for a very short time or at lower temperatures should be suitable to capture the effects of small excess values. Experimentally, lower temperatures but longer times are easier to realize as one can expect a large scatter when samples are annealed just for very short time intervals.

In Fig. 4 we present the first results of the hardness evolution as a function of the annealing time for temperatures lower than 823 K. It can be seen that the hardness increase is smaller for lower annealing temperatures. Independent of the annealing temperature, a similar behavior to that at 823 K (see Fig. 1b) is observed. The hardness rises quickly before it seems that it levels off at a certain plateau value. Surprisingly even at the lowest annealing temperature of 343 K (~ 0.2 T_m) a significant hardness increase can be observed. Although it is very unlikely that segregation takes place at such a low annealing temperature within 5 minutes, a detailed study has to be carried out to clarify this result.
Apart from this study, several other results also suggest, that segregation is not essential for the hardening. For example, nc samples showed pronounced hardening when cyclically loaded at, for nc metals, relatively large plastic strain amplitudes [10]. This behavior was also observed for the nc austenitic steel used in the present study [11]. The reason for the cyclic hardening seems to be an exhaustion of easy mobile dislocations with increasing number of cycles. An in-situ straining TEM study on UFG Al points in the same direction. Stresses to operate a grain boundary source were found to be much larger than those necessary to overcome an obstacle, most likely an impurity [12].

Figure 4. RT hardness of isothermally annealed nc 316L samples as a function of the annealing time.

3. Hardening by annealing – a grain size related phenomena?
As mentioned earlier, hardening by annealing was reported for a wide range of pure metals as well as alloys. Despite this fact, several severely deformed materials do not show a hardness increase upon annealing. In contrast, they show rather constant hardness values until grain growth takes place. One example is UFG high purity Ni (99,99 %) processed by HPT, where no hardening occurs during annealing, see Fig. 5. When Ni powder (3-7 µm particle size) was consolidated and subsequently HPT deformed a slight hardening during annealing takes place. The higher initial hardness of the powder consolidated samples indicates a smaller grain size for this set of samples, as impurities and oxides on the powder surface slow down boundary mobility, thus shifting the minimum grain size achievable by HPT to smaller sizes. Annealing of the Ni powder in air (400 °C for 10 minutes) results in an increase of the oxide content of the powder and to a further reduction of the grain size after HPT. Interestingly, these samples showed an even larger hardness increase upon annealing. From these results one could expect hardening by annealing to be a grain size dependent phenomenon. However, the impurity level of the powder and the bulk material were different. Although the results in section 2) indicate that this might not explain the different extent of hardening, experiments on samples of the same impurity/alloying content would be more meaningful to interpret. As the minimum grain size achievable in HPT can also be modified by changing the deformation temperature, samples of identical nominal composition but a different grain size can easily be processed. To do so, a Pt5Ru (concentration in wt-%) alloy produced by arc melting was deformed by HPT at 77 K, RT and 573 K. The alloy contains only a single phase after deformation as confirmed by TEM. SAED patterns captured after annealing also did not show signs of the formation of additional phases. Grain sizes of the three samples were calculated by analyzing EBSD data. After deformation, the samples having different grain sizes but the same composition were subjected to isochronal heat treatments (30 minutes) in a temperature range up to 773 K. The results are summarized in Fig. 6.
It can be seen that with a decrease of the deformation temperature also the hardness of the alloys increases, which is in good agreement with grain size measurements. Upon annealing, for the samples deformed at 77 K and RT pronounced hardening can be seen, whereas for the samples deformed at 573 K the hardness increase is almost negligible. Similar to the results in Fig. 5, the relative hardness increase ΔH is increasing with decreasing grain size. By plotting the hardness increase ΔH as a function of the grain size, a clear dependency can be seen as shown in Fig. 6b). These results strongly indicate that hardening by annealing will only occur below a threshold value of the grain size, which is 220 nm for the Pt5Ru alloy under investigation. As can be expected from Fig. 5, also for Ni, hardening will occur only below a certain grain size.

The occurrence of the hardening mechanism only below a specific grain size might further rule out a strong contribution of segregation to the strengthening. Since for all Pt5Ru samples the global composition remains the same, only the excess values of segregated solute might be different. For a given annealing temperature one can expect the diffusion length, i.e. the distance from which solute can be transferred to the grain boundaries, to be similar for all three sets of samples. Only the surface area over which the solute can be distributed drastically increases with decreasing grain size (~ 1/d). Based on this estimation one would expect larger solute excess values for the samples having the largest grain size. The estimation of ‘smaller is cleaner’ was also experimentally validated [13]. In the case of a strong correlation between segregation and strengthening, one would expect a significantly enhanced strengthening of the samples having the largest excess of segregated solute – the opposite of what is observed, see Fig. 6.
The reason for this grain size dependent behavior is yet not clear. It seems that this transient behavior must be related to intrinsic features of crystal plasticity being dominant in the grain size regimes below and above the observed threshold value. One could expect, for grains coarser than a critical value, intragranular sources to be still active after the heat treatment, while with decreasing grain size a transition to intergranular dislocation sources takes place. As outlined above, this requires much higher stress levels.

4. Conclusion and Outlook
Hardening by annealing is frequently observed in nc materials. Although this phenomenon has been known for several years the role of segregated impurities or solute to the strengthening is yet not clear. Additionally, several UFG materials show hardening by annealing while others do not. The present study presents experimental findings to clarify the raised questions. The findings lead to the following conclusions:

1) Formation of second phase particles and large variations of the type of segregated solute do not have an influence on the mechanical properties of the investigated nc steel
2) Hardening by annealing can occur at relatively low homologous temperatures
3) Hardening by annealing occurs only in materials with grain sizes below a material specific threshold value

Although the combination of APT and mechanical datasets provided deeper insights to rationalize the origin of the strengthening, the effect of small excess values still remains unclear. However, as significant hardening within short time intervals occurs, further in depth studies are promising to resolve this question. Apart from these observations the impact of this hardening mechanism, specifically of different boundary chemistries, on other mechanical properties such as ductility or fracture toughness will bear further scrutiny.

Acknowledgements
Financial support by the FWF Austrian Science Fund within project number 24141-N19 and the European Research Council under ERC Grant Agreement No. 340185 USMS is gratefully acknowledged.

References
[1] Huang X, Hansen N, and Tsuji N 2006 Science 312 249
[2] Ma E, Shen T and Wu X 2006 Nat. Mater. 5 515
[3] Shen T D et al 2007 Acta Mater. 55 5007
[4] Valiev R Z et al 2010 Scripta Mater. 63 949
[5] Van Swygenhoven H, Derlet P M and Frøseth A G 2006 Acta Mater. 54 1975
[6] Hasnouui A, Van Swygenhoven H and Derlet P M 2002 Acta Mater. 50 3927
[7] Li J C M 2006 Phys. Rev. Lett. 96 215506
[8] Renk O et al 2015 Scripta Mater. 95 27
[9] Chih-Chun Hsieh and Wu W 2012 ISRN Metallurgy 2012 732471
[10] Moser B et al 2006 Scripta Mater. 54 1151
[11] Renk O, Hohenwarter A and Pippan R 2012 Adv. Eng. Mater. 14 948
[12] Mompou F et al 2013 Acta Mater. 61 205
[13] Terwilliger C D and Chiang Y 1995 Acta Metall. Mater. 43 319