Turk, C.; Kellezi, G.; Leitner, H.; Staron, P.; Gan, W.; Clemens, H.; Primig, S.:

B2 order transformation in a Fe - 25 at% Co - 9 at% Mo alloy.

In: MRS Online Proceedings Library. Vol. 1760 Warrendale, PA: Materials Research Society, 2014. 175 - 180.

First published online by Materials Research Society: 01.07.2015

https://dx.doi.org/10.1557/opl.2015.117

B2 order transformation in a Fe – 25 at% Co – 9 at% Mo alloy

Christoph Turk [1], Gert Kellezi [2], Harald Leitner [2], Peter Staron [3], Weimin Gan [3], Helmut Clemens [1] and Sophie Primig [1]

[1] Department of Physical Metallurgy and Materials Testing, Montanuniversitaet Leoben, Roseggerstraße 12, 8700 Leoben

[2] Böhler Edelstahl GmbH & Co KG, Mariazellerstraße 25, 8605 Kapfenberg, Austria

[3] GEMS, Helmholtz-Zentrum Geesthacht, Max-Planck-Str.1, D-21502 Geesthacht, Germany

ABSTRACT

The ternary system Fe - 25 at% Co - 9 at% Mo shows an age hardening behavior similar to aluminum alloys. After solution annealing followed by rapid quenching, the Fe-Co-matrix is hardened during subsequent aging through precipitation of the intermetallic μ-phase $(Fe,Co)_7Mo_6$. In aged condition the entire Mo content is present in coarse primary and fine μ-phase particles and, therefore, the matrix consists exclusively of 71 at% Fe and 29 at% Co. The binary system Fe-Co shows a transformation from the disordered bcc structure to the ordered B2 structure between 25 and 72 at% Co at a critical ordering temperature ranging from room temperature to 723°C. As a consequence, the remaining overaged matrix in the Fe - 25 at% Co - 9 at% Mo system should also show such a transition. However, an ordered phase is brittle and, thus, not wanted for many applications. Better mechanical properties in terms of ductility can be achieved with a partially or fully disordered phase. Such a state can be obtained by rapid quenching from temperatures above the critical ordering temperature. In this study such an approach was implemented on the ternary Fe - 25 at% Co - 9 at% Mo alloy. The effect of different cooling rates on the mechanical properties was investigated by means of hardness testing. The actual ordering transition of the Fe - 29 at% Co matrix was determined with differential scanning calorimetry and neutron diffraction.

INTRODUCTION

Solution annealing and subsequent aging of the ternary Fe - 25 at% Co - 9 at% Mo alloy cause the formation of nm-sized $(Fe,Co)_7Mo_6$ μ-phase precipitates, which leads to significant hardening of this alloy. However, overaging decreases the strengthening effect as the precipitates start to coarsen. In this condition, the matrix consists of 71 at% Fe and 29 at% Co only [1]. It is known that in Fe-Co alloys a bcc↔B2 order transition takes place between 25 at% and 72 at% Co. There, the ductile disordered bcc α-matrix transforms at a critical ordering temperature into a brittle B2 ordered α'-matrix showing a CsCl lattice. Moreover, rapid quenching of such alloys promotes a disordered matrix with a reduced hardness [2]. It has been

reported for a Fe - 30 at% Co (Fe30Co) alloy that rapid quenching with water leads to a completely disordered Fe30Co matrix [3]. Since the overaged matrix of the investigated alloy exhibits almost a Fe30Co composition [1], it is assumed that in our system such an order transition will also take place. To validate this order phenomenon, annealing heat treatments in the disordered bcc-region followed by different cooling operations were carried out. In the first attempt the mechanical properties were characterized by hardness testing. In addition to this, differential scanning calorimetry and neutron diffraction experiments were used to characterize the mechanism responsible for the individual hardness level in the differently cooled samples.

EXPERIMENTAL DETAILS

The investigated material is a powder metallurgically processed alloy. Samples with dimensions of 10 x 10 x 10 mm^3 were cut from the bar material. All heat treatments were carried out in a CARBOLITE tempering furnace in a Ar-inert gas atmosphere at 800°C for 30 min. The cooling variation was done by water quenching (1000 K/s), oil quenching (60 K/s), air cooling (2 K/s), and furnace cooling (0.2 K/s). Moreover, one sample was cooled in the furnace with a cooling rate of 0.5 K/s from 800 to 600°C followed by cooling with 0.083 K/s from 600°C to 500°C and finally with 0.5 K/s from 500°C to room temperature (slow cooled). All samples were cut, ground and polished prior to hardness testing and metallographic examinations. HRC150 hardness measurements were done on a EMCO M4R-075 hardness tester, whereby an average hardness value from three indents on each sample condition was calculated. Scanning electron investigations (SEM) were conducted with a ZEISS EVO 50 in back-scatter electron mode. Differential scanning calorimetry (DSC) was carried out using a SETARAM LABOSYS EVO instrument calibrated with the melting points of several pure elements [4]. The DSC samples were prepared from the heat treated samples by cutting discs with a diameter of 3.4 mm and a thickness of 0.35 mm. Al_2O_3 crucibles were used both for sample and reference. The reference crucible was left empty. The DSC experiments were carried out with constant heating rates of 6 K/min and 30 K/min in a dynamic Ar-atmosphere with a flow-rate of 20 ml/min. Neutron diffraction experiments were performed at the STRESS-SPEC diffractometer operated by FRM II and HZG at the Heinz Maier-Leibnitz Zentrum (MLZ), Garching, Germany. The neutron beam had a wavelength of 1.603 Å and an experimental setup with a GE 311 monochromator and a 25” collimator was used [5]. The exposure time was kept constant with 10 minutes.

RESULTS AND DISCUSSION

Figure 1 shows a SEM image in back-scatter mode of the material in the as received condition. The two-phase microstructure of the ferritic Fe – 29 at% Co matrix and the coarse $(FeCo)_7Mo_6$ μ-phase particles is evident. The grain size of the Fe - 29 at% Co matrix is below 1 μm. In [2,3] it is reported that an improved ductility can be gained by a smaller grain size. Therefore, the heat treatment conditions were chosen to obtain a homogenously disordered bcc matrix with a similar grain size as in the as-received condition. Moreover it has been reported from [1] that annealing at this temperature does not lead to dissolution of the μ-phase particles. The influence of different cooling conditions on the hardness of the material is plotted in figure 2.

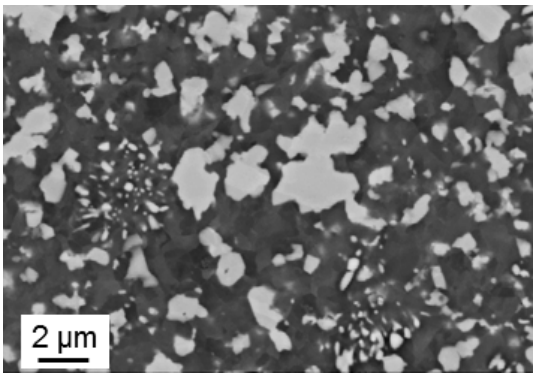

Figure 1. SEM image of the Fe - 25 at% Co - 9 at% Mo in the as-received condition in back-scatter mode. The coarse primary µ-phase particles appear in light gray and the Fe - 29 at% Co matrix in dark gray.

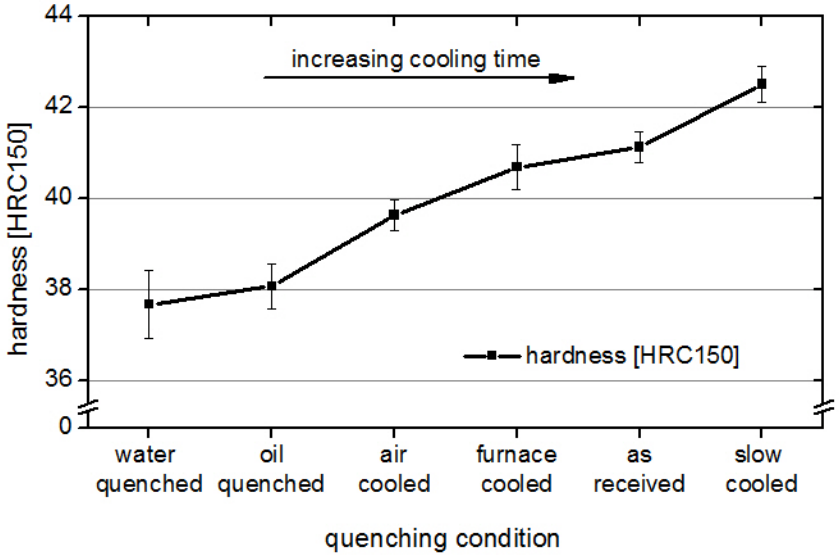

Figure 2. Hardness values as a function of the cooling rate. All specimens were cooled from 800°C after a holding time of 30 min. The hardness level increases with decreasing cooling rate. Remarkably, the lowest hardness can be achieved by water quenching.

The hardness values of the differently cooled samples show a distinct trend. Water and oil quenching led to low hardness values of about 38 HRC. With increasing cooling time, e. g. decreasing cooling rate, the hardness increases until it reaches a value of 41 HRC, which is close to that of the as-received condition. The highest hardness can be obtained in case of the slow cooled sample. The obtained results are in good agreement with the work of Zhao and Baker [3] who investigated Fe30Co alloys. These authors also found an enhanced ductility and lower strength for fast quenched tensile samples. It is known [2] that rapid quenching from a temperature above the critical ordering temperature leads to a decrease in strength and to an enhanced ductility, whereas slow cooling causes increase in strength and loss of ductility. Thus, it is tempting to suppose that such an ordering transition is responsible for the observed hardness change in the present quenching experiments. If such a phase transition takes place, however the ordering reaction should be detectable by means of DSC. Due to the fact that the order-disorder

transition is a completely reversible mechanism, only heating experiments were carried out using the different cooled samples as starting material. For that purpose the water quenched, the as-received and the slow cooled samples were selected for the DSC experiments. The heat flow behavior plotted versus the sample temperature for constant heating rates of 6 K/min and 23 K/min can be seen in figures 3a and b, respectively.

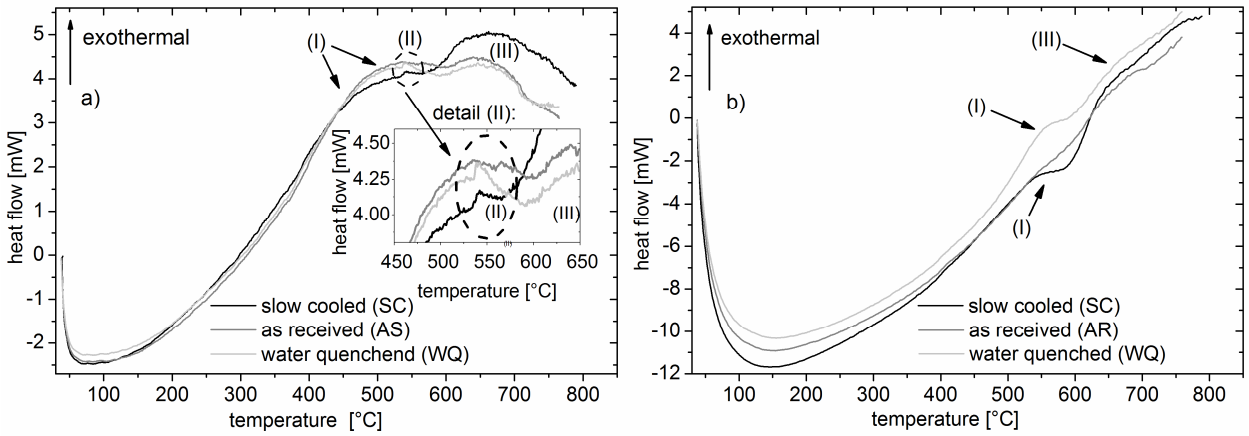

Figure 3. a) DSC heating experiments with a heating rate of 6 K/min. Note the exothermal pre-peak at about 550°C. The order-disorder transition takes place at 590°C; b) DSC heating experiments with a heating rate of 23 K/min. The "550°C peak" is not visible at this higher heating rate.

All DSC-heating experiments with 6 K/min in figure 3a show an endothermal behavior above 450°C (I) followed by two distinct exothermal peaks with onsets at 540°C (II) and 590°C (III). The endothermal change of the heat flow (I) could arise from an ordering process as the temperature approaches the critical ordering temperature. Measurements of the long-range order parameters of Fe30CoPt/Pd alloys using in situ-neutron diffraction have revealed that the degree of order increases when the temperature approaches the critical ordering temperature as ordering takes place [6]. The water quenched and the slow cooled samples show a exothermal peak at 540°C (II) which could be attributed to the so-called 550°C anomaly as reported in [2,7,8]. Although there is profound experimental evidence for this phenomenon since many physical properties change at this temperature, no clear explanation for this effect has been published so far [2]. It was assumed, however, that this effect could arise from a magnetic contribution [9]. Nevertheless, this peak is not evident in the heating curve of the as-received sample. The second exothermal peak with an onset at 590°C (III) could relate to the order-disorder transition because the critical ordering temperature according to the binary FeCo phase diagram after Okuma [10] is approximately 590°C for Fe - 29 at% Co. Thus, it is expected that these peaks originate from an order-disorder transition. In addition to this, figure 3b shows the heating experiment with a heating rate of 23 K/min. In these experiments it is obvious that the heating rate is too fast to resolve all peaks described previously. The first endothermal peak (I) could be resolved in case of the water quenched and slow cooled sample, but the disorder-order transition (III) could only be assumed from the shape of the curve. The as-received condition shows a slight endothermal behavior compared to the other material conditions. Furthermore, the 550°C peak could not be detected in any heating experiment. Therefore, the 550°C anomaly is suggested to be a diffusion controlled process, as already proposed by [8]. These experiments revealed that a change in the heat flow occurred at temperatures where an order-disorder transition in a Fe - 29 at% Co alloy

should take place. However, direct evidence of order in this alloy is still required. Therefore, additional neutron diffraction experiments were carried out. Neutron diffraction has an advantage in the case of Fe and Co, since these elements exhibit different scattering lengths for neutrons. As a consequence, the structural order of Fe and Co atoms can be easier resolved by neutron diffraction than by X-ray diffraction [11]. The neutron diffraction patterns of the water quenched and the slow cooled sample are displayed in figure 4.

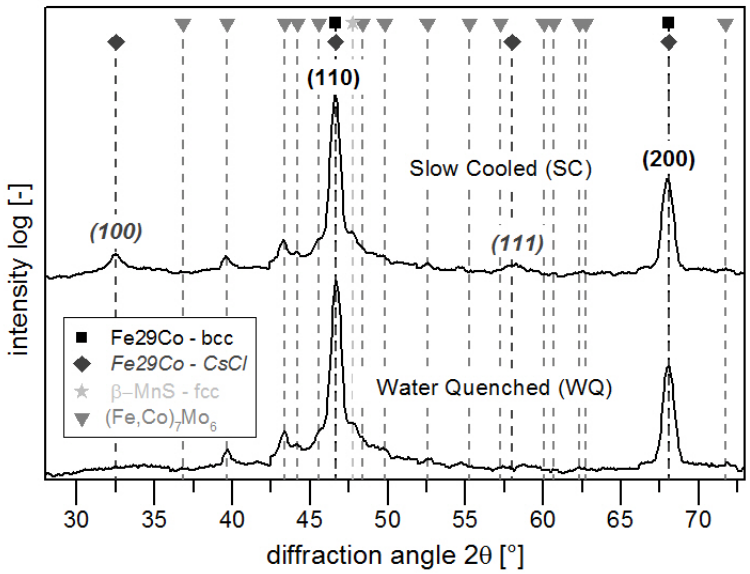

Figure 4. Neutron diffraction patterns of the slow cooled and the water quenched specimen with a Fe - 29 at% Co matrix. The superlattice reflections arising from B2 ordered FeCo domains in the matrix are visible in the pattern of the slow cooled sample, whereas these reflections are not present in the pattern of the water quenched condition. Evidently, this sample must be completely disordered.

The neutron diffraction patterns of both samples show peaks from the disordered Fe - 29 at% Co matrix marked in the pattern with (110) and (200). However, the pattern of the slow cooled sample exhibits additional peaks at 32.5° and 57.5°. These peaks can be attributed to (100) and (111) superlattice reflections of B2 ordered FeCo domains [11]. The results of these experiments prove, that the slow cooled Fe - 29 at% Co matrix exhibits B2 ordered regions. These superlattice reflections are not resolved in the pattern of the water quenched sample, therefore, it is tempting to speculate that the water quenching led to a completely disordered Fe - 29 at% Co matrix. This assumption is in good agreement with literature [3,12,13], where water quenching has led to a complete disorder of the samples, too.

CONCLUSIONS

In this work, the order-disorder transition of the Fe - 29 at% Co matrix in a Fe - 25 at% Co - 9 at% Mo alloy could be verified by hardness testing, differential scanning calorimetry and neutron diffraction experiments. It was shown, that the ordering causes an increased hardness of the alloy when slowly cooling from the disordered bcc α-phase field

region. Moreover, the experiments proved that annealing above the critical ordering temperature, followed by accelerated cooling, caused a softening of the alloy due to the suppression of ordering within the Fe - 29 at% Co matrix.

ACKNOWLEDGEMENT

The author would like to thank Mr. Gerhard Hawranek for the SEM investigations and Dr. Emanuel Schwaighofer for helpful discussions regarding the neutron diffraction experiments.

REFERENCES

1. H. Leitner, M. Schober, H. Clemens, D. Caliskanoglu, F. Danoix, *Int. J. Mater. Res.* **99**, 367 (2008).
2. T. Sourmail, Prog. *Mater. Sci.* **50**, 816 (2005).
3. L. Zhao, I. Baker, *Acta Metall. Mater.* **42**, 1953 (1994).
4. S. Vyazovkin, A. K. Burnham, J. M. Criado, L. A. Pérez-Maqueda, C. Popescu, N. Sbirrazzuoli, *Thermochim. Acta* **520**, 1 (2011).
5. M. Hofmann, W. M. Gan, J. Rebelo-Kornmeier, M. Schöbel*, Neutron News* **24,** 14 (2013).
6. R. Gilles, M. Hofmann, F. Johnson, Y. Gao, D. Mukherji, C. Hugenschmidt, P. Pikart, *J. Alloys Compd.* **509**, 195 (2011).
7. T. Yokoyama, T. Takezawa, Y. Higashida, *Trans. Japan Inst. Met.* **12**, 30 (1971).
8. S. K. H. Asano, Y. Bando, N. Nakanishi, *Trans. Japan Inst. Met.* **8**, 180 (1967).
9. V. I. Gomankov, D. F. Litvin, A. A. Loshmanov, B. G. Lyashchenko, I. M. Puzei, *Sov. Phys.-Cryst.* **7**, 788 (1963).
10. I. Ohnuma, H. Enoki, O. Ikeda, R. Kainuma, H. Ohtani, B. Sundman, K. Ishida, *Acta Mater*. **50**, 379 (2002).
11. C. Shull, S. Siegel, *Phys. Rev.* **75**, 1008, (1949).
12. Y. I. Mal'tsev, V. I. Gorman'kov, I. M. Puzey, A. D. Skokov, *Phys. Met. Met.* **43**, 47 (1977).
13. R. Gilles, M. Hofmann, Y. Gao, F. Johnson, L. Iorio, M. Larsen, F. Liang, M. Hoelzel, B. Barbier, *Metall. Mater. Trans. A* **41**, 1144 (2009).