Non-destructive measurement of the tungsten content in the binder phase of tungsten heavy alloys

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Abstract

Measurement of the magnetic properties is well-established to non-destructively monitor composition and microstructure of cemented carbides. The present study demonstrates that this method can also be applied to ferromagnetic tungsten heavy alloys. Compositional changes during heat treatment may have effects on the magnetic properties of W-Ni-Fe heavy alloys, as an example, which would allow for simple non-destructive measurement. We report that increasing tungsten content in Ni-Fe(-W) samples and higher annealing temperatures for *Densimet 180*® grade 95W-Ni-Fe heavy alloy samples cause a decrease of their respective weight-specific saturation magnetization. XRD analyses show that higher heat treatment temperatures result in larger lattice parameters of the binder phase. Likewise, larger amounts of tungsten dissolved in the nickel-iron samples also widen the γ-Ni-Fe lattice. This suggests that the decrease in saturation magnetization of heavy alloys annealed at higher temperatures is caused by more dissolved tungsten in the binder phase. A relationship between saturation magnetization and tungsten content in the binder could be established through the Ni-Fe(-W) samples with known amounts of tungsten. In view of these results, we propose saturation magnetization measurements as a simple non-destructive tool for additional quality control in the production of ferromagnetic tungsten heavy alloys.

Keywords

Tungsten heavy alloy, W-Ni-Fe, composite material, liquid-phase sintering, saturation magnetization, heat treatment, XRD

Introduction

Liquid-phase sintered composite materials made of tungsten, nickel and other transition metals are commonly known as Tungsten Heavy Alloys (WHAs). Due to their unique combination of very high density, outstanding mechanical properties and excellent machinability, they are used in a wide range of high-performance applications, e.g. for balancing weights in aerospace and automotive industry,

collimators and radiation shielding components, vibration-damping tool holders, kinetic energy penetrators, oscillating weights and sports equipment [1, 2]. WHAs are composed of nearly pure body-centered cubic (bcc) tungsten grains embedded in a ductile face-centered cubic (fcc) matrix phase (Fig. 1).

Although full density may be achieved through solid-state sintering, the presence of a liquid phase during sintering of WHAs is essential for obtaining their typical structure and properties [3]. Among the multitude of processes occuring during liquid-phase sintering, solution-reprecipitation of tungsten plays a major role. Upon melting of the binder powders, tungsten is dissolved in the newly formed liquid phase. Dissolution occurs preferentially at small grains and convex surfaces, whereas reprecipitation of tungsten is favored at large grains and concave surfaces [4]. In the long run, this effect causes growth and rounding of the tungsten grains. When the liquid phase solidifies during cooling, some tungsten remains dissolved in it and will therefore affect the properties of the binder.

W-Ni-Fe, one of the most commonly used WHA types, is weakly ferromagnetic [5] and therefore, considering its structure, in some way comparable to cemented carbides, typically composed of hard tungsten carbide grains in a ductile cobalt matrix. For cemented carbides, coercivity and saturation magnetization measurements are well-established non-destructive methods of monitoring chemical composition and microstructure [6]. A correlation between tungsten grain size and coercivity (as known for tungsten carbide in cemented carbides) was reported for W-Ni-Fe heavy alloys by Danninger *et al.* [7]. However, very little information can be found in the literature about their magnetization behavior [5, 8] and, to the best of the authors' knowledge, no connection between saturation magnetization and applied heat treatment has been described for W-Ni-Fe. In this work, we intend to fill this gap by investigating the effects of heat treatment on the saturation magnetization of W-Ni-Fe and exploring whether saturation magnetization measurements may therefore be used for determining the tungsten content in the binder phase of ferromagnetic WHAs.

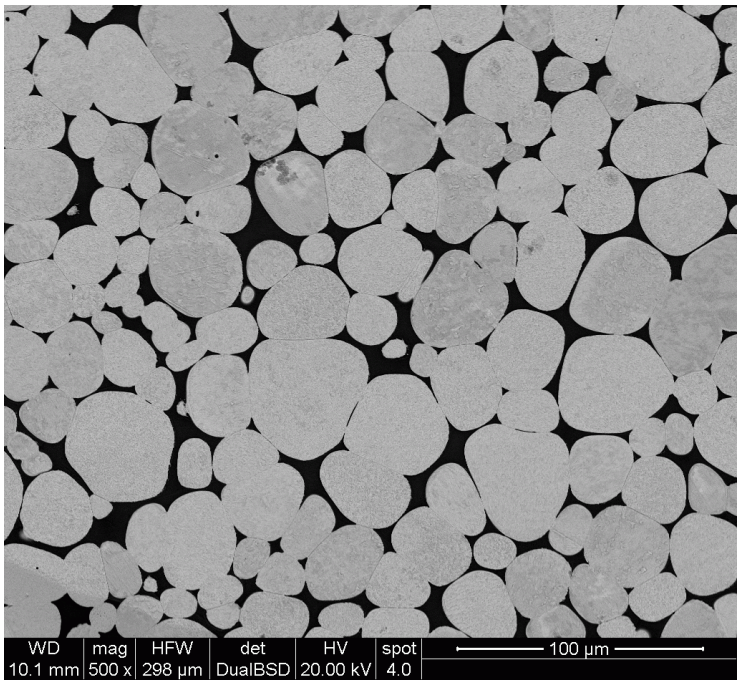

Figure 1: Typical structure of a 95W-Ni-Fe heavy alloy (BSE image, tungsten particles are bright, binder phase is dark)

Experimental

Small *Densimet 180*® grade 95W-Ni-Fe heavy alloy samples (approximately 10x10x5 mm³ in size) were produced by *Plansee Composite Materials* via liquid-phase sintering in hydrogen atmosphere at an isothermal sintering temperature of 1773 K (1500 °C). Specimens were then vacuum annealed for 10 hours at 1373, 1473 and 1573 K (1100, 1200 and 1300 °C), respectively. Furthermore, in order to exclude effects other than compositional changes, a stepwise heat treatment was performed involving a 10-hour heat treatment at 1573 K followed by 10 hours at 1373 K. The linearized cooling rate after annealing was approximately 10 K/min down to 873 K (600 °C).

Nickel-iron(-tungsten) specimens with defined amounts of dissolved tungsten between 0 and 20 wt.% were produced by mixing elemental powders (from the same powder batches and at the same nickel-to-iron ratio as for the W-Ni-Fe samples) and melting the powder mixtures by heating to 1773 K (1500 °C) in hydrogen atmosphere with an isothermal dwell time of 1 hour before cooling (nominal heating and cooling rates were 10 K/min each).

Weight-specific saturation magnetization σ_s was determined for all samples with a Koerzimat CS 1.096 instrument (*Institut Dr. Foerster GmbH & Co. KG,* Germany) using the withdrawal method in accordance with IEC 60404-14. X-ray diffractograms were recorded by the TU Wien X-Ray Center with an XPert Pro MPD diffractometer (*PANalytical B.V.,* Netherlands) using Bragg-Brentano geometry for 2θ angles from 5 to 100° and Cu K_α irradiation. Rietveld refinement calculations were performed using the HighScore Plus software by PANalytical.

Results

Weight-specific saturation magnetization values of *Densimet 180*® samples measured in the as-sintered state and after vacuum heat treatment at varying temperatures are given in Fig. 2 and Table I. It can be seen that the saturation magnetization decreases with higher temperatures. Stepwise heat treatment at 1573 K followed by 1373 K resulted in saturation magnetization values comparable to those of samples annealed at 1373 K only, suggesting that the microstructural changes introduced during heat treatment are not permanent. Likewise, weight-specific saturation magnetization values measured for Ni-Fe(-W) samples with 0 to 20 % dissolved tungsten are shown in Fig. 3. The red line indicates the calculated values assuming that nickel-iron and tungsten were hypothetically present as fully separate phases (i.e. if the decrease in saturation magnetization was solely caused by the lower amount of ferromagnetic nickel-iron phase due to the addition of tungsten), based on the saturation magnetization of the pure nickel-iron alloy.

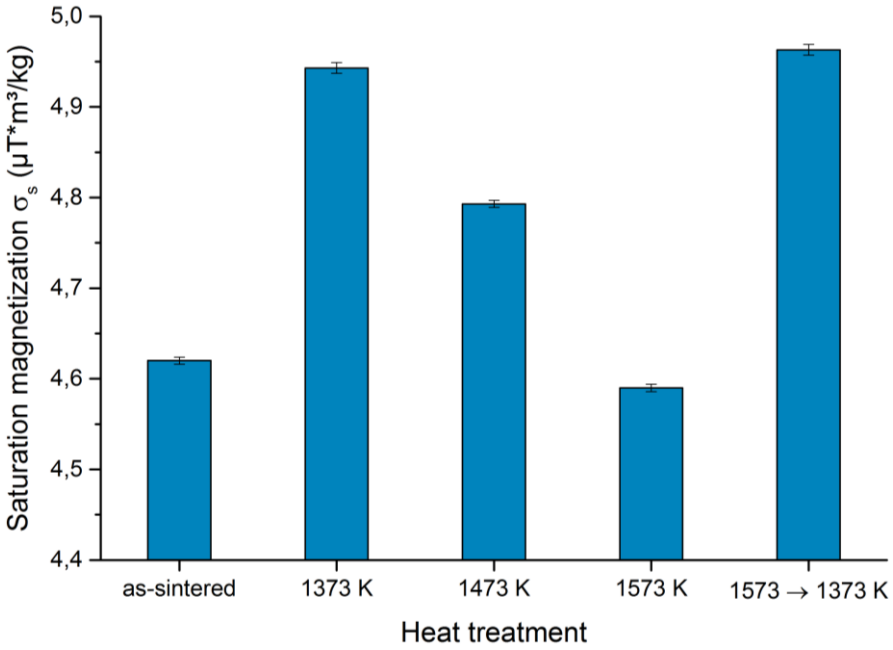

Figure 2: Weight-specific saturation magnetization of *Densimet 180*® samples after different vacuum heat treatments

Table I: Weight-specific saturation magnetization of *Densimet 180*® samples after different vacuum heat treatments

Heat treatment	Saturation magnetization σ_s
as-sintered	4.620 ± 0.004 µT*m³/kg
1373 K (1100 °C)	4.943 ± 0.006 µT*m³/kg
1473 K (1200 °C)	4.793 ± 0.004 µT*m³/kg
1573 K (1300 °C)	4.590 ± 0.004 µT*m³/kg
1573 → 1373 K	4.963 ± 0.006 µT*m³/kg

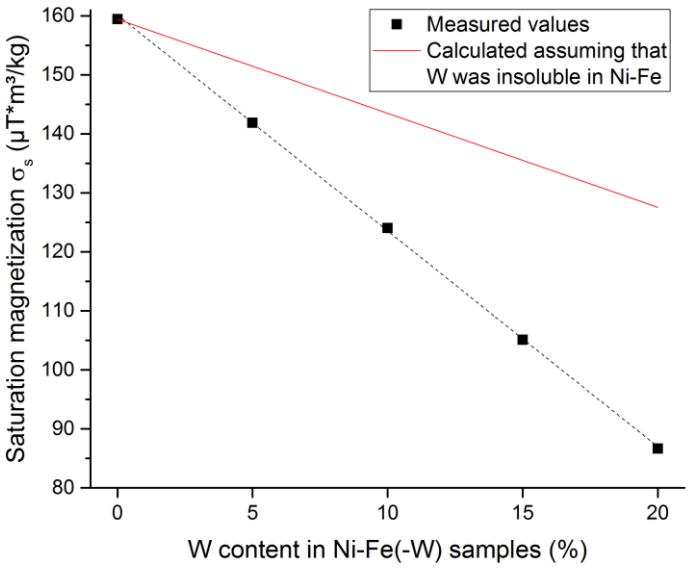

Figure 3: Weight-specific saturation magnetization of Ni-Fe(-W) samples with varying tungsten contents

X-ray diffractograms (Fig. 4) show that the Ni-Fe(-W) specimens are monophasic, as only the peaks of fcc γ-Ni-Fe (Ref. code 00-047-1417 [9]) are present. The five visible peaks in all diffractograms can be assigned to the (111), (200), (220), (311) and (222) lattice planes of γ-Ni-Fe, confirming that tungsten is fully dissolved. With increasing amounts of dissolved tungsten, the peaks are shifted slightly towards lower diffraction angles. According to the Bragg equation

$$n\lambda = 2d \sin\theta \tag{1}$$

lower 2θ-angles correspond to an increase in the interplanar distance d and therefore an increase in the lattice parameter a of the cubic unit cell according to

$$d_{hkl} = \frac{a}{(h^2+k^2+l^2)^{0.5}} \tag{2}$$

with h, k, l being the Laue indices of the lattice plane.

Lattice parameters of the γ-Ni-Fe(-W) phase were obtained for each sample applying Rietveld refinement to the recorded diffractograms. As can be seen from Fig. 5, these calculations confirmed that dissolved tungsten widens the fcc lattice by approximately 0,141 ± 0,009 pm for each percent of tungsten added.

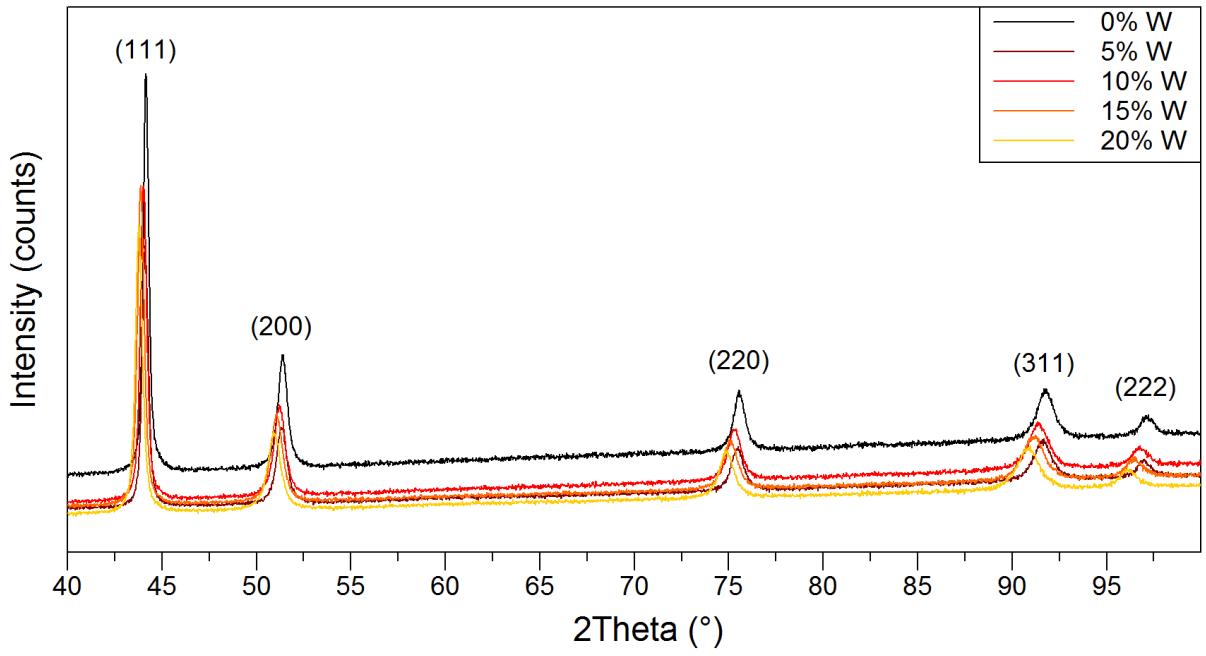

Figure 4: X-ray diffractograms of Ni-Fe(-W) samples with varying tungsten contents

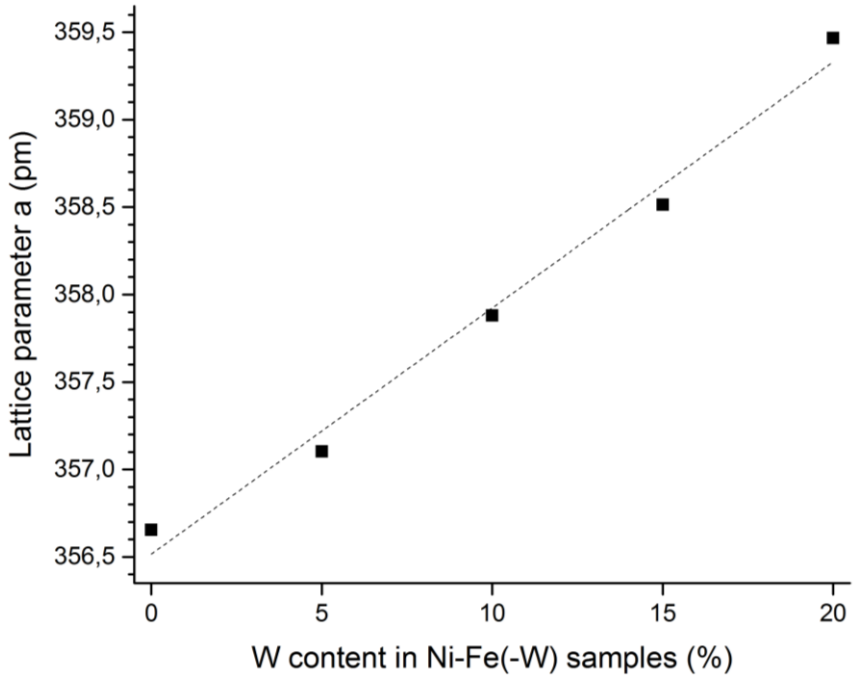

Figure 5: Lattice parameters of Ni-Fe(-W) samples with varying tungsten contents

Discussion

The production of WHAs usually comprises liquid-phase sintering under hydrogen atmosphere, since the reduction of oxides present in the metal powders is essential for obtaining the excellent mechanical properties of heavy alloys [10]. Since hydrogen is dissolved in the binder phase during sintering, post-sintering heat treatments are performed in vacuum or argon atmosphere in order to avoid hydrogen embrittlement. Besides the removal of hydrogen, heat treatment is also beneficial for homogenizing the chemical composition of the binder phase [11].

The presented results show that the magnetic properties of W-Ni-Fe heavy alloys are clearly influenced by the vacuum heat treatment performed after sintering. Higher temperatures lower the resulting saturation magnetization. This effect, however, appears to be non-permanent, as annealing at 1573 K followed by 1373 K gives nearly the same results as heat treatment at 1373 K only. We therefore conclude that this phenomenon is caused by a larger amount of tungsten dissolved in the nickel-iron binder phase of samples annealed at higher temperatures. Saturation magnetization after heat treatment at 1573 K is comparable to the as-sintered state. This is somewhat surprising, as sintering was performed at 1773 K. One possible explanation is that the tungsten diffusion in the solidified binder during cooling is still rather fast at temperatures close to the solidus temperature of the nickel-iron phase. Since the binder in 95W-Ni-Fe alloys is very thin, the diffusion paths for dissolved tungsten are short (cf. Fig. 1), which may allow for a comparably quick precipitation from the oversaturated solid solution. This could likely lead to a similar tungsten content in the binder phase and thus to a saturation magnetization similar to that of samples annealed at 1573 K.

Since tungsten itself is paramagnetic, the weak ferromagnetism of W-Ni-Fe heavy alloys is caused by the thin nickel-iron binder phase (which, however, contains certain amounts of dissolved tungsten) surrounding the almost pure tungsten particles. The saturation magnetization of ferromagnetic materials

generally depends on the purity of the material and is lowered by non-magnetic solutes [12]. It is well known that dissolved tungsten and carbon in the Co binder phase of WC-Co cemented carbides lower their saturation magnetization [6], therefore it appears reasonable to assume that such an effect also occurs in structurally similar W-Ni-Fe heavy alloys.

Indeed, it could be shown that the weight-specific saturation magnetization of Ni-Fe(-W) samples is lowered as more tungsten is dissolved. This linear decrease in saturation magnetization is stronger than what could be expected assuming (hypothetically) that tungsten was insoluble in the nickel-iron phase (indicated by the red line in Fig. 3).

Given that the magnetism of W-Ni-Fe is caused solely by the binder phase, the data shown in Fig. 3 allows for an approximation of the amount of dissolved tungsten. Linear regression gives a correlation between the tungsten concentration in the binder (%W) and the weight-specific saturation magnetization σ_s according to

$$\%W = \frac{160.137 - \sigma_s}{3.658} \quad (3)$$

Since only 5 % of the *Densimet 180*® heavy alloy is nickel-iron, the measured σ_s values from Table I must be multiplied by a factor of 20 in order to allow for comparison with the monophasic Ni-Fe(-W) specimens. Taking this into account and inserting the respective σ_s values in Equation 3, the tungsten concentrations given in Table II are obtained. It must be noted that this method is merely an approximation, as the dissolution of tungsten in the binder phase will inevitably affect the mass and volume percentage of the binder in the WHA. For exact calculations, the tungsten concentration would have to be known in advance (rendering the calculations themselves pointless).

Table II: Tungsten concentration in the binder phase of *Densimet 180*® samples after different vacuum heat treatments calculated from saturation magnetization measurements

Heat treatment	Tungsten concentration in binder phase
as-sintered	18.5 %
1373 K (1100 °C)	16.8 %
1473 K (1200 °C)	17.6 %
1573 K (1300 °C)	18.7 %
1573 → 1373 K	16.6 %

In the X-ray diffractograms of the Ni-Fe(-W) samples (Fig. 4), a slight peak shift towards lower 2θ angles is clearly visible as the amount of dissolved tungsten increases, indicating a widening of the fcc lattice. Similar to Equation 3, Equation 4 describes the mathematical correlation between the tungsten concentration and the lattice parameter *a* depicted in Fig. 5. Tungsten concentrations calculated with this method are listed in Table III.

$$\%W = \frac{a - 356.5163}{0.1407} \quad (4)$$

Table III: Tungsten concentration in the binder phase of *Densimet 180*® samples after different vacuum heat treatments calculated from X-ray diffractograms

Heat treatment	Tungsten concentration in binder phase
1373 K (1100 °C)	14.4 %
1473 K (1200 °C)	16.8 %
1573 K (1300 °C)	17.5 %

Comparing the two methods, it is apparent that the calculations based on the lattice parameters derived from XRD analyses give lower concentrations than those based on the saturation magnetization measurements. This might be due to larger uncertainty of the calculated lattice parameters values compared to the saturation magnetization data. For instance, the results of the Rietveld calculations depend to a certain extent on the refinement procedure used. Although the same refinement steps and parameters were used for all calculations, absolute values are assumed to be less precise than those obtained through saturation magnetization measurements. Furthermore, residual stresses in the composite material might influence the peak positions. Still, the trend of higher heat treatment temperatures leading to larger amounts of tungsten in the binder phase is confirmed by both methods.

Preliminary results from ongoing experiments on the influence of powders provided by different suppliers indicate that the raw materials used have a certain but minor influence on the measured saturation magnetization of WHAs [13], which may be due to different levels and types of impurities in the metal powders. For exact absolute quantification, calibrations linking the saturation magnetization to the tungsten concentration in the binder phase would probably have to be created for each combination of tungsten, nickel and iron powders. While this is, of course, always a possible option, simply monitoring relative differences of ferromagnetic WHA parts from the same batch should already be sufficient to detect anomalous parts. Since saturation magnetization measurements are fast, non-destructive, independent of specimen geometry and automatable, they could readily be incorporated into existing quality control routines of heavy alloy producers.

Conclusion

This work demonstrates that higher heat treatment temperatures lead to a non-permanent decrease in weight-specific saturation magnetization of W-Ni-Fe heavy alloys. XRD analyses reveal that this phenomenon is caused by increasing tungsten concentrations in the nickel-iron binder phase. Using *Densimet 180*® as an example, it was shown that the tungsten content in the binder phase of WHAs can be calculated from their magnetic properties, based on saturation magnetization measurements of Ni-Fe(-W) with defined amounts of dissolved tungsten. Although the absolute saturation magnetization may to some minor extent depend on the raw materials used, this method is ideal for detecting anomalous parts in batches of ferromagnetic WHAs by simply monitoring relative differences and could therefore be a valuable tool for quality control.

Acknowledgements

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