Cementite in the Fe–N–C system

Von der Fakultät Chemie der Universität Stuttgart zur
Erlangung der Würde eines Doktors der Naturwissenschaften (Dr. rer. nat.)
genehmigte Abhandlung

vorgelegt von

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Tag der Einreichung:	28.08.2008
Tag der mündlichen Prüfung:	18.11.2008

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MAX-PLANCK-INSTITUT FÜR METALLFORSCHUNG, STUTTGART
STUTTGART, 2008

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1
General Introduction

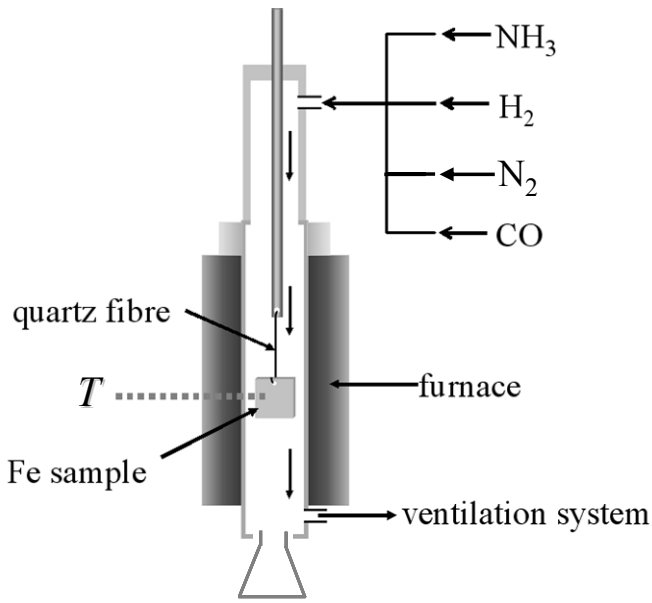
In technical applications, layer/substrate systems are of increasing importance since they may result in positive properties, which cannot be achieved by (simple) bulk materials. A layer/substrate system combines two components, the substrate material and the layer on top of the substrate. The aim is to realise a material combination which benefits from the positive properties of both the substrate such as e.g. ductility and the positive properties of the layer such as e.g. hardness and corrosion resistance. This materials combination may overcome negative properties such as e.g. the limited hardness of the substrate and the brittleness of the layer. Such layer/substrate systems can be generated by different processes, e.g. by thermochemical heat treatments due to chemical reactions of a reactive gas atmosphere with the substrate material [1-3].

Gaseous nitriding, gaseous carburising and gaseous nitrocarburising are such thermochemical heat treatments, which are of pronounced technical importance since the beginning of the twentieth century. These processes lead, due to chemical reactions of the reactive gas atmosphere with the substrate material, to a concerted change of the chemical composition of the (usually) iron-based workpieces. This concerted change of the chemical composition can lead to the formation of a diffusion zone within which nitrogen and/or carbon are either dissolved in the octahedral sites of the iron *bcc*-lattice or are bound to alloying elements. The diffusion zone, which can extend several hundreds of micrometers, is responsible for a considerable enhancement of the fatigue endurance of the iron-based workpiece [4]. Furthermore, under certain circumstances (high activities of nitrogen and/or carbon in the gas atmosphere), the change of the chemical composition of the iron-based workpiece can lead to the generation of hard, wear and corrosion resistant surface compound layers with thicknesses up to several

tenths of micrometers [5]. Gaseous nitriding and gaseous nitrocarburising are performed at temperatures in the range of 773 K – 843 K, i.e. below the binary/ternary eutectoid temperatures (ferritic regime) of the Fe–N/Fe–N–C solid solution [2]. Upon gaseous nitriding and/or gaseous nitrocarburising, nitrogen and/or carbon are diffusionally incorporated into the surface region of an iron-based workpiece. In contrast, upon carburising, carbon is incorporated into the surface region of an iron-based workpiece at usually much higher treatment temperatures in the range of 1173 – 1273 K. Due to these higher treatment temperatures, which are located in the austenitic regime, considerable changes of the dimensions of the iron-based workpiece result, which is in contrast to gaseous nitriding/nitrocarburising.

In the present work, thermochemical heat treatments were performed in a vertical quartz tube furnace. At the top part of the quartz-tube furnace, the gas inlet was located, where ammonia, hydrogen, carbon monoxide and nitrogen were inserted into the furnace. The specimen was positioned by a sample stage and a quartz fibre in the middle of the quartz-tube furnace where the process temperatures, controlled within ± 1 K, prevailed. The quartz-tube furnace was, at its bottom part, equipped with a water container for quenching the specimens to room temperature. After the desired treatment time, the quartz fibre was mechanically destroyed and the specimen dropped into the quenching facility to retain microstructural states which were produced at the treatment temperature.

(a)



(b)

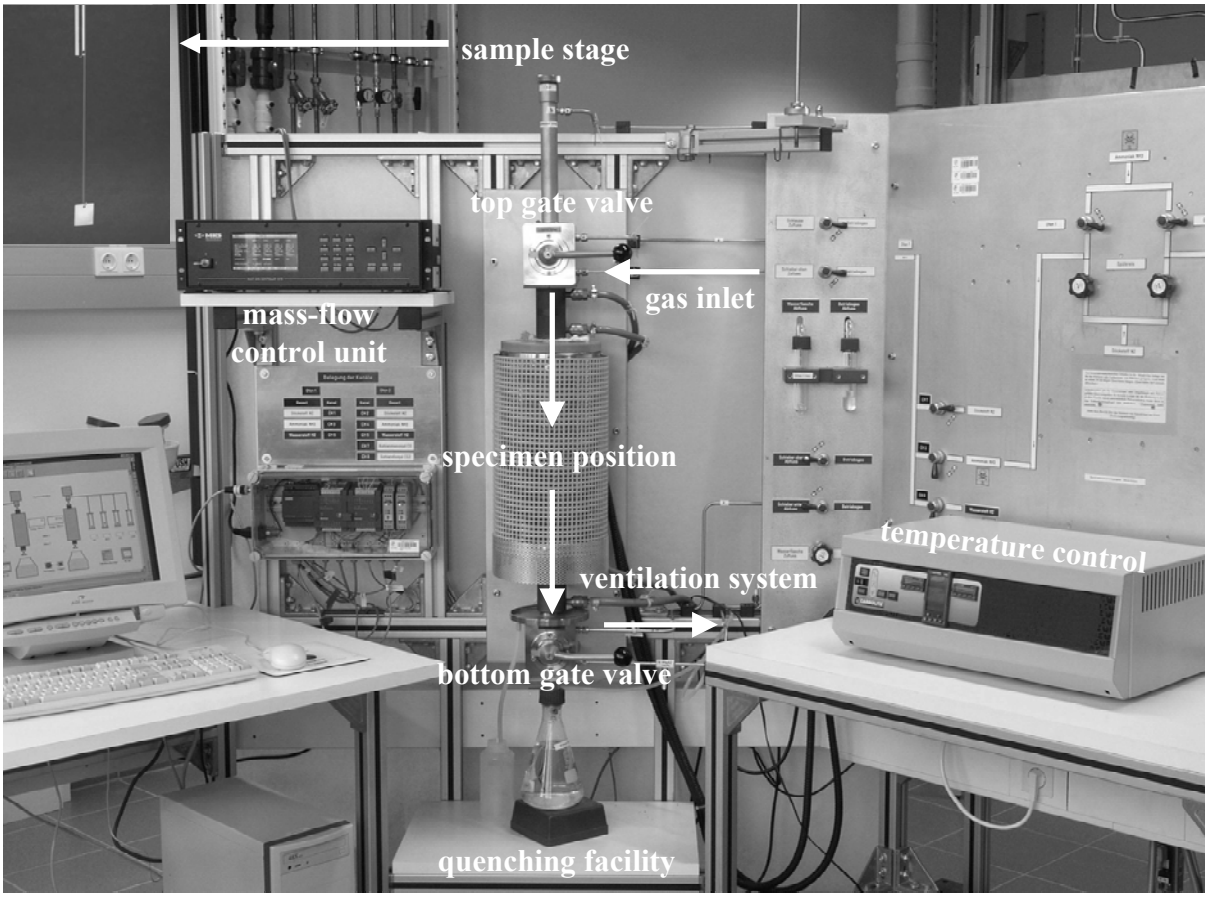


Fig. 1.1: (a) Schematic representation and (b) real image of the nitriding/nitrocarburising/carburising facility. The arrows indicate the gas inlet, the direction of the gas flow and the gas outlet. At the bottom part of the nitriding/nitrocarburising/carburising facility, the quenching facility was located, which consists of a water container (flushed with nitrogen).

After the thermochemical heat treatment (in the present work gaseous nitriding/nitrocarburising), a diffusion zone develops within which α''-$Fe_{16}N_2$ [6-10] or γ'-Fe_4N_{1-y} precipitates can be formed. On top of this diffusion zone a compound layer develops which can, depending on the process parameters (treatment temperature, treatment pressure, treatment time, composition of the gas atmosphere) consist of different phases [11,12]. Usually the compound layer consists of γ'-Fe_4N_{1-y} and/or ε-$Fe_3(N,C)_{1+x}$ [13] but, also cementite can form within the compound layer [14,15] (cf. *chapter 2*) coexisting with γ'-Fe_4N_{1-y} and ε-$Fe_3(N,C)_{1+x}$.

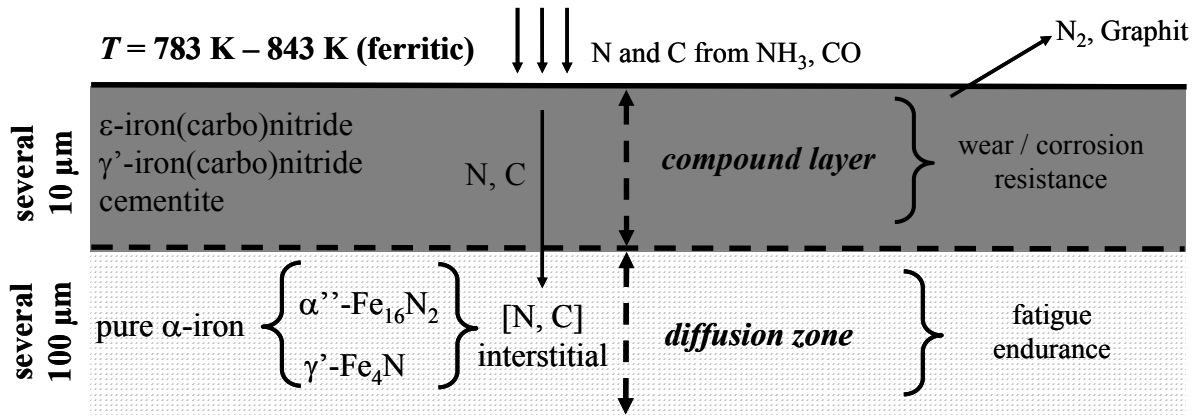


Fig. 1.2: Schematic illustration, which indicates that the surface region of an iron-based workpiece can be subdivided into a diffusion zone and a compound layer after gaseous nitriding/nitrocarburising. These contain, depending on the process parameters, different phases. Nitrogen and/or carbon are provided by the ammonia- and/or carbon monoxide-containing gas atmosphere. Ammonia and/or carbon monoxide dissociation occurs at the surface of the specimen. Due to a gradient of the chemical potential of nitrogen and/or carbon from the surface to the substrate, nitrogen and/or carbon are diffusionally incorporated into the surface region of the iron-based workpiece.

The formation of massive cementite compound layers upon gaseous carburising is usually accompanied by severe sooting and cementite disintegration, so-called metal dusting [16]. Therefore, the generation of massive cementite compound layers is not trivial. In the literature it is reported that due to the addition of H_2S to the carburising gas atmosphere, sooting and metal dusting can be suppressed [17-20]. Moreover, there are hints that the addition of ammonia to the carburising gas atmosphere may delay or even suppress sooting and metal dusting [21].

Although gaseous nitrocarburising is widely applied in industrial processes, many open questions remain. The aim of this work is to generate massive cementite compound layers on ferrite substrates. Furthermore, the present work shall answer some open questions concerning cementite in the Fe–N–C system.

8

Summary

8.1 Introduction

Gaseous nitriding, gaseous carburising and gaseous nitrocarburising are thermochemical heat treatments, which are of pronounced technical importance since the beginning of the twentieth century. The substrate (iron-based materials, mostly steels) reacts with the gas atmosphere, and, due to the chemical reactions that take place, a concerted change of the chemical composition of the iron-based workpieces results. This can lead to the formation of a diffusion zone with a thickness of several hundreds of micrometers, within which nitrogen and/or carbon (provided by the gas atmosphere) are either dissolved in the octahedral sites of the iron *bcc*-lattice or are bound to alloying elements. This diffusion zone is responsible for a considerable enhancement of the fatigue endurance of the iron-based workpiece. Furthermore, the concerted change of the chemical composition of the iron-based workpiece can lead to the generation of hard, wear- and corrosion-resistant surface compound layers, which can extend several tens of micrometers.

Gaseous nitriding and gaseous nitrocarburising are usually performed at temperatures in the range of 773 K – 843 K. The process temperature is located below the binary/ternary eutectoid temperatures of the Fe–N/Fe–N–C solid solutions i.e. in the ferritic regime. Whereas the nitriding and/or the nitrocarburising gas atmosphere provide nitrogen and/or carbon, the carburising gas atmosphere only provides carbon. These are incorporated into the surface region of an iron-based workpiece by diffusion processes. Gaseous carburising is usually performed at much higher treatment temperatures in the range of 1173 – 1273 K. Therefore, the process temperature is located in the austenitic regime, which results in - in contrast to gaseous

nitriding/nitrocarburising - considerable changes of the dimensions of the iron-based workpiece.

Within the diffusion zone, which developed after the thermochemical heat treatment (in the course of the present work gaseous nitriding/nitrocarburising), α''-$Fe_{16}N_2$ or γ'-Fe_4N_{1-y} precipitates can be formed. The compound layer (located on top of the diffusion zone), which may develop after the thermochemcial heat treatment under certain circumstances (high activities of nitrogen and/or carbon) can, depending on the process parameters (treatment temperature, treatment pressure, treatment time, composition of the gas atmosphere) consist of different phases. The compound layer is usually composed of γ'-Fe_4N_{1-y} and/or ε-$Fe_3(N,C)_{1+x}$ but, also cementite can form within the compound layer coexisting with γ'-Fe_4N_{1-y} and ε-$Fe_3(N,C)_{1+x}$.

The formation of massive cementite compound layers on ferrite substrates is not trivial. Cementite formation upon gaseous carburising is usually accompanied by severe sooting and cementite disintegration, so-called metal dusting. It was reported in the literature that due to the addition of H_2S to the carburising gas atmosphere, sooting and metal dusting can be suppressed. There were even hints in the literature that the addition of ammonia to the carburising gas atmosphere may delay or even suppress sooting and metal dusting.

Although thermochemical heat treatments such as gaseous nitrocarburising are widely applied in industrial processes, many open questions remain. The present work aims on the one hand at the generation of massive cementite compound layers on ferrite substrates. On the other hand, the present work shall answer some open questions concerning cementite in the Fe–N–C system.

8.2 Experimental Procedure

By cold-rolling an α-iron cast rod (99.98 gew.-% Fe) on both sides, an iron foil of 1 mm thickness was produced. The rectangular specimens (20 mm × 25 mm) to be thermochemically heat treated were cut from this iron foil, afterwards ground and polished. Prior to the thermochemical heat treatment, the specimens were recrystallised for 2 h at 973 K under a reductive hydrogen atmosphere.

9
Zusammenfassung in deutscher Sprache

9.1 Einleitung

Gasnitrieren, Gascarburieren und Gasnitrocarburieren sind thermochemische Wärmebehandlungsverfahren von Eisenbasismaterialien, meist Stählen, die seit dem 20. Jahrhundert von großer technologischer Bedeutung sind. Hierbei wird durch eine chemische Reaktion des Substratmaterials mit einer reaktiven Gasatmosphäre, die Stickstoff und/oder Kohlenstoff bereitstellt, eine gezielte Veränderung der chemischen Zusammensetzung des Eisenbasismaterials erzielt. Dieses kann zur Erzeugung einer sogenannten Diffusionszone führen, in der primär Stickstoff und/oder Kohlenstoff in den Oktaederlücken des kubisch-raumzentrierten Eisens eingelagert werden können. Die Diffusionszone, die mehrere hundert Mikrometer dick sein kann, ist für eine erhebliche Verbesserung der Ermüdungsbeständigkeit des Eisenbasismaterials verantwortlich. Darüber hinaus kann unter bestimmten Reaktionsbedingungen (hohe Stickstoff- und/oder Kohlenstoffaktivität in der Gasatmosphäre) die gezielte Veränderung der chemischen Zusammensetzung des Eisenbasismaterials zur Erzeugung einer harten, verschleißfesten und korrosionsbeständigen Verbindungsschicht an der Probenoberfläche führen, die mehrere zehn Mikrometer dick sein kann.

Die Prozesse des Gasnitrierens und des Gasnitrocarburierens werden für gewöhnlich im Temperaturbereich zwischen 773 K und 843 K durchgeführt, d.h. man befindet sich dabei unterhalb der binären/ternären eutektoiden Temperatur (ferritisch) des Fe–N/Fe–N–C-Mischkristalls. Im Verlauf der Behandlungsreaktion werden Stickstoff und/oder Kohlenstoff mittels Diffusionsprozessen im Oberflächenbereich des Eisenbasismaterials eingelagert. Dem gegenüber steht der Prozess des Gascarburierens bei dem bei einer Behandlungstemperatur von 1173 K – 1273 K, also

bei einer wesentlich höheren Behandlungstemperatur, Kohlenstoff im Oberflächenbereich des Eisenbasismaterials eingelagert wird. Durch diese höheren Behandlungstemperaturen - man befindet sich im Austenitgebiet - kommt es im Gegensatz zum Gasnitrieren und Gasnitrocarburieren zu einem erheblichen Verzug der zu behandelnden Probe.

Innerhalb der Diffusionszone, die sich nach Beendigung der thermochemischen Wärmebehandlung (im Rahmen dieser Arbeit handelt es sich dabei um Gasnitrieren und Gasnitrocarburieren) ausgebildet hat, können α''-$Fe_{16}N_2$- oder γ'-Fe_4N_{1-y}-Ausscheidungen entstehen. Die ausgebildete Verbindungsschicht kann in Abhängigkeit der Prozessparameter (Behandlungstemperatur, Behandlungsdruck, Behandlungsdauer, Zusammensetzung der reaktiven Gasatmosphäre) aus unterschiedlichen Phasen bestehen. Gewöhnlich besteht die erzeugte Verbindungsschicht aus γ'-Fe_4N_{1-y} und/oder ε-$Fe_3(N,C)_{1+x}$, aber auch Zementit kann neben diesen beiden erwähnten Phasen in der Verbindungsschicht koexistieren.

Die Erzeugung von reinen, massiven Zementitschichten mittels Gascarburierens hingegen wird immer von starker Verrußung und der Zementitzersetzung begleitet, welche als „metal dusting“ bezeichnet wird. Auf Grund dessen kann die Erzeugung von reinen, massiven Zementitschichten als nicht gerade trivial bezeichnet werden. In der Literatur wurde berichtet, dass die Verrußung und die Zementitzersetzung („metal dusting“) durch die Zugabe von H_2S zur aufkohlenden Gasatmosphäre unterdrückt werden können. Darüber hinaus gibt es in der Literatur Hinweise darauf, dass auch die Zugabe von Ammoniak zur aufkohlenden Gasatmosphäre die Verrußung und die Zementitzersetzung verlangsamen oder gar unterdrücken können.

Trotz der Tatsache, dass Gasnitrocarburieren in industriellen Prozessen weit verbreitet ist, gibt es viele unbeantwortet Fragen. Das Ziel dieser Arbeit soll einerseits die Erzeugung von reinen, massiven Zementitschichten auf ferritischen Reineisensubstraten sein. Andererseits sollen bisher unbeantwortete Fragen beantwortet werden, die im Zusammenhang mit Zementit als einer Phase des Fe–N–C Systems stehen.

9.2 Experimentelle Vorgehensweise

Aus einem Reineisenabguss (99,98 gew.-% Fe) wurde durch beidseitiges Kaltwalzen eine Eisenfolie der Dicke von 1 mm hergestellt. Daraus wurden die zu behandelnden rechteckigen Proben (20 mm × 25 mm) herausgeschnitten, anschließend geschliffen, poliert und gereinigt. Vor der thermochemischen Wärmebehandlung wurden die Proben für 2 h bei 973 K unter einer reduzierenden Wasserstoffatmosphäre rekristallisiert.

Für die thermochemische Wärmebehandlung wurden die Proben mit Hilfe einer Probenstange und eines daran befestigten Quarzfadens in die Mitte eines vertikal angeordneten Mehrzonenofens eingebracht, in dem die Behandlungstemperatur (geregelt innerhalb ± 1 K) vorlag. Am oberen Ende des Mehrzonenofens befindet sich der Gaseinlass, an dem Ammoniak, Wasserstoff, Kohlenstoffdioxid und Stickstoff, gesteuert durch Massedurchflussregler, in den Mehrzonenofens eingeleitet werden können. Am unteren Ende des Mehrzonenofens befindet sich eine Abschreckeinheit, die aus einer Wasserflasche besteht, die mit Stickstoff gespült wird. Nach Ablauf der gewünschten Behandlungsdauer kann der Quarzfaden mechanisch abgetrennt werden und die Probe fällt direkt in die Abschreckeinheit. Dadurch kann die Mikrostruktur, die bei der Behandlungstemperatur vorlag, bei Raumtemperatur stabilisiert werden.

Die behandelten Proben wurden mit unterschiedlichen Methoden charakterisiert. Die Untersuchung der Mikrostruktur erfolgte mittels Lichtmikroskopie an Querschliffen. Zur Phasenanalyse wurden die Elektronenrückstreubeugung sowie die Röntgenpulverdiffraktometrie (CoK_α-Strahlung) herangezogen. Zur röntgenographischen Spannungsmessung wurde Synchrotronstrahlung verwendet. Das entsprechende Diffraktometer war mit einer Eulerwiege ausgestattet und arbeitete in Parallelstrahlgeometrie.