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**Optimization of the Critical Content of Tramp
Elements in Ultra-High Strength Silicon Chromium
Spring Steels through Thermomechanical Treatment**

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1 SCOPE OF THE THESIS

This work is concerned with improving the mechanical properties of quenched and tempered martensitic steel, that is the alloy 54SiCr6 and is used for automotive coil springs. Steels for light-weight applications as in the case of automotive springs have to fulfil contradictory requirements. Automotive springs have to be optimized for minimum weight, for optimum package, maximum robustness and minimum cost. From these criteria the material selection criteria for spring steels can be derived (Fig. 1). These are high yield strength to allow higher stress levels in the elastic range, high endurance limit for a long operation and a minimum toughness to avoid catastrophic failure due to load shocks. Furthermore, most manufacturers and most industrial standards require a good ductility level. High ductility level usually corresponds to a good toughness and apart from that is needed for cold forming of coil spring of small diameter.

In this work, special attention is paid to the role of the impurity elements phosphorous, copper and tin. Phosphorous is known to deteriorate the toughness and ductility, but the concentration limits are not known for 54SiCr6 and manufacturing processes to minimize the negative effect on the mechanical properties are absent. Copper and tin are elements that are introduced into steels due to the increased usage of scrap in steel production. Most investigators have concentrated on the effect of copper on the hot liquid embrittlement. In the present work the effect of copper and tin on the mechanical properties of tempered martensite was investigated.



Fig. 1 Material selection criteria for coil springs

The ductility and toughness of the final part are affected by the concentration and distribution of the impurity elements in the bulk material. The distribution of these elements is a result of the process parameters, i.e. of the history of the material from the melt to the final process step. In this work the composition and the key heat treatment parameters were varied systematically and the resulting mechanical properties and the microstructure were characterized. The composition was varied changing the concentration of phosphorous, copper and tin. For each phosphorous and copper and tin concentration two melts were compared, one without vanadium and one with addition of vanadium.

Because the existing heat treatment used to manufacture springs, namely austenitization, quenching and tempering does not exploit the full potential of the existing steel grade, an additional degree of freedom for material optimization was introduced by austenite deformation prior to quenching. Such treatments that combine deformation and heat treatment are called thermomechanical treatment or thermomechanical processing. Former research in this field has proven that superior properties can be achieved after deformation of austenite prior to quenching (Hensger and Bernstein 1984, Zouhar 1984, Peters and Kaspar 1997, Wettlaufer and Kaspar 2000b). In this work the specific boundary conditions for manufacturing coil springs were considered for the new thermomechanical routes. The main goal was to develop a concept for a thermomechanical treatment that produces improved final material properties independent of impurity level.

In brief, the objective of the project from an industrial point of view was

- 1) to determine the impurity level limits below which the required properties are produced,
- 2) and to develop a novel treatment to increase the strength level above the strength of springs used today (around 2000 MPa) and maintain the ductility and fatigue properties without additional cost for a higher purity level.

The scientific motivation of the work is to extend the knowledge about the embrittling mechanisms in martensitic steels and the dependence of tempered martensitic microstructure on the grain structure of the parent austenite phase. The authors cited above ascribed the improvements in mechanical properties observed after thermomechanical treatment mainly to the substructure of the austenite grains prior to quenching. In commercially used alloys, this substructure can not be investigated due to the transformation the steel undergoes upon cooling. Instead iron nickel model alloys (Hensger and Bernstein 1984) and the final martensite have been investigated. It has been shown qualitatively that thermomechanical

treatment refines the martensite and increases the fraction of lath martensite (Hensger and Bernstein 1984, Peters 1997). Additionally, carbides formed during tempering are finely dispersed (Hensger and Bernstein 1984) and the internal stresses generated during cooling are reduced (Peters 1997). Furthermore, the role of impurity elements has been discussed, but is controversial (Hensger and Bernstein 1984, Zouhar 1984, Peters et al. 1996, and Wettlaufer 2000). In the present work we used modern techniques to understand the martensitic microstructure and its relation to the mechanical properties. Martensitic structural units that define the mechanical properties were investigated by crystal orientation imaging techniques using electron diffraction. Special attention was paid to the influence of the austenite condition and the martensite morphology, size distribution of structural units and the distribution and morphology of carbides at prior austenite grain boundaries.

2 THEORETICAL BACKGROUND

2.1 FERROUS MARTENSITE

Martensite, named after the German metallurgist Adolf Martens, exhibits the highest hardness of the phases known in iron based alloys. Martensitic microstructures can only be produced if the transformation to mixtures of ferrite and cementite or other phases is avoided. The high hardness associated with high strength, fatigue resistance, and wear resistance are the main reasons for the technological importance of martensitic steels. The properties can be varied by further annealing steps to obtain a desirable combination of strength and ductility or toughness. These characteristics are responsible for the variety of alloys and applications for ferrous martensite. Today, martensitic steels are used for light-weight structures in automotive and aerospace industry as springs, shafts, landing gears. They are used as ball and roller bearings.

The specific strength of martensitic steels is higher than that of the strongest aluminium alloys used in the aerospace industry. Only in cases where the stiffness (ratio of elastic modulus to density) requirements dominate, aluminium and titanium alloys become superior.

In order to produce martensite the diffusional transformations from austenite to other phases must be suppressed. Therefore all the martensite is produced by “quenching” from the austenite to a temperature below which martensite forms (*martensite start temperature M_S*). Quenching is a commonly used terminology, and can include cooling in water (low carbon steel), in oil or in even in air (high alloyed tool steel). The critical cooling speed in a given steel to obtain a fully martensitic microstructure depends very strongly on the chemical composition, especially on the content of carbon, on the austenite grain size, and on the austenite substructure or defect structure.

In this chapter first the characteristics of austenite-martensite transformation together with the transformation microstructures is presented. Main focus is placed on those factors influencing the transformation and microstructure and thus changing the mechanical properties. In the subsequent section then the mechanical properties as a result of the microstructure are explained.

2.1.1 MARTENSITE TRANSFORMATION

The martensite transformation is diffusionless, athermal and is characterized by a shear mechanism, where many atoms move cooperatively and (almost) simultaneously. This type of transformation implies necessarily a fixed orientation relationship between the parent and the final phase. The orientation relationships between the parent phase and daughter phase have been found for different alloy systems and have been reviewed in different papers (Ray and Jonas 1990, Morito 2003, Nolze 2004, Guo et al. 2004). The crystallography of martensitic transformation is described further below. A second consequence of the cooperative movement of atoms is that the composition of the daughter martensite phase is exactly the same like the parent austenite phase.

For a particular steel, the athermal reaction takes place in a specific temperature range. The transformation is accompanied by abrupt change of physical properties such as volume and electrical resistance. The reaction initiates at the *martensitic start temperature* M_S and ceases at the *martensitic finish temperature* M_f . Ideally, at the latter temperature all the austenite should have transformed to martensite, but in practice, a small fraction of the austenite does not transform. This is called *retained austenite*. Alloying elements influence the M_S temperatures of steels. A number of equations have been generated which relate the martensitic start temperature with steel composition. A review of these equations is given in (Krauss 1990 and Ohtani 1992). If the M_f drops below room temperature significant fraction of retained austenite is present at room temperature. Alloying elements that stabilize the austenite increase the fraction of retained austenite.

The plane in the austenite on which the martensite forms and grows is the *habit plane*. It affects the initiation and progress of the transformation and it determines the microstructural arrangement of the martensite crystals within one prior austenite grain (Krauss and Marder 1971, Davies and Magee 1971).

The carbon atoms in martensite as well as in the parent austenite occupy octahedral interstices. The average unit cell of both lattices expands in a linear manner as a function of carbon content. In contrast to the austenitic solid solution of iron and carbon where the enlarged lattice remains face centred cubic, carbon atoms in martensite produce nonsymmetrical distortions and convert the body centred cubic into body centred tetragonal structure (Cohen 1962). Because the lattice distortion caused by interstitial carbon in bct-iron is non-symmetrical (Fig. 2) it has been referred to as “distortion dipole” (Cohen 1962). The

tetragonality, defined as the ratio between the c- and a-axis depends on the carbon concentration (given in mass %, after Roberts, in Cohen 1962):

$$\frac{c}{a} = 1.000 + 1.045 C \quad (\text{Equation 1})$$

In iron-carbon systems the solubility of carbon in a bcc system is greatly exceeded after martensite transformation. Because the partition of carbon between ferrite and cementite through diffusion has been suppressed, the martensite is a metastable phase. If the martensite is heated to temperatures, where the carbon atoms become mobile, the carbon atoms move out of the octahedral sites and form clusters of carbon atoms or carbides (2.1.4.2). As a consequence the tetragonality is successively lost and the martensite is replaced by a mixture of ferrite and cementite.

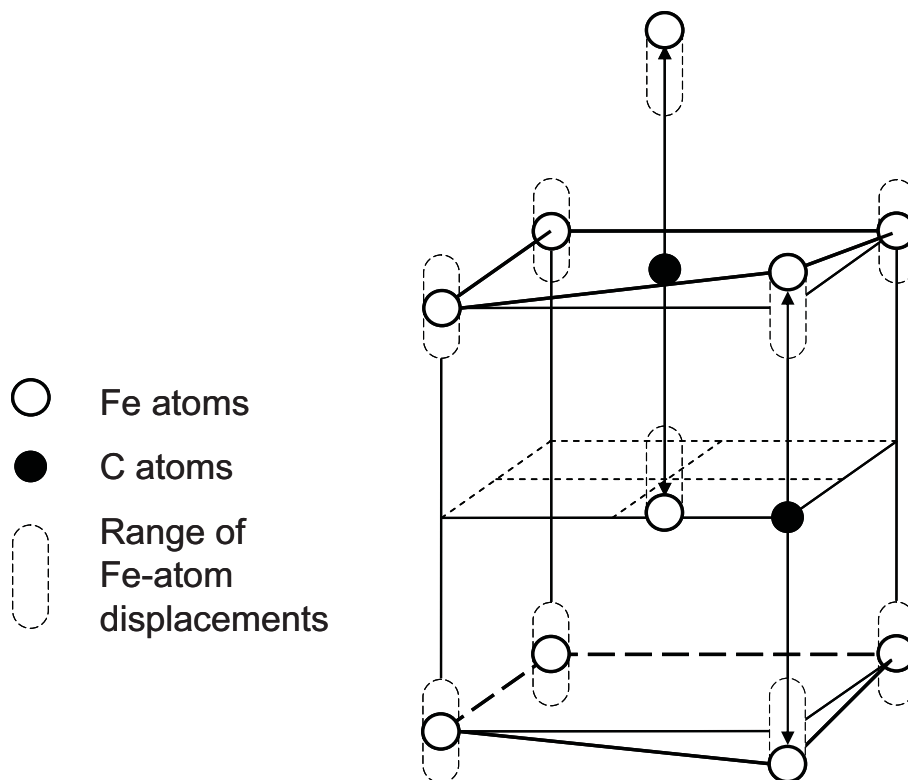


Fig. 2 Representation of iron-atom displacement due to the presence of carbon in body-centred tetragonal martensite lattice (after Lipson and Parker, Cohen 1962).

Generally the *lattice transformation* causes rotation of the final lattice from the habit plane. Fig. 3 shows how a number of cells of the parent crystal a) are transformed to a new lattice b). The grey vertical dashed lines represent the unrotated, undistorted habit plane. To satisfy the constraints of the surrounding matrix and maintain the shape, a *lattice invariant deformation* occurs that conserves the macroscopic shape of the phase. The lattice invariant deformation satisfies – on a macroscopic scale – the requirements of an unrotated, undistorted habit plane. It takes place by slip or by twinning as shown in Fig. 3 c) or d) respectively. When slip is the main mode of accommodation during lattice invariant deformation dislocations are introduced at the austenite-martensite interface. Additionally a high dislocation density is observed in the fine structure within the plates or lath (Swarr 1976). Does the transformation occurs at high temperatures (M_S around 450°C) as in the case of low- or medium-carbon steels then slip is the main lattice invariant deformation, while at lower M_S temperatures the main mechanism is twinning.

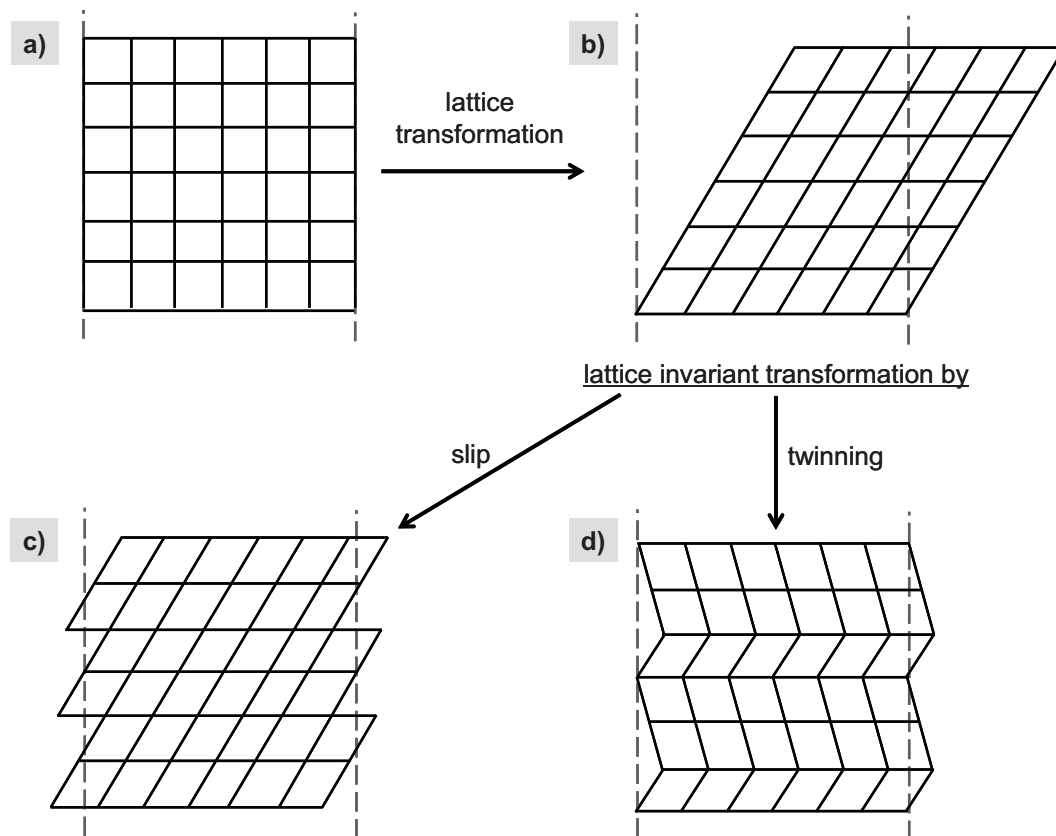


Fig. 3 Schematic diagram of martensitic transformation