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Low-temperature martensitic transformation in tool steels in relation to their deep cryogenic treatment

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Abstract

The low-temperature martensitic transformation in steel X153CrMoV12 containing (mass%) 1.55C, 11.90Cr, 0.70V, 0.86Mo is studied using dilatometry, Mössbauer spectroscopy, X-ray diffraction, mechanical spectroscopy and transmission electron microscopy. Some additional measurements were carried out on steel X220CrMoV13-4. It is shown that, in contrast to the widely known absence of martensitic transformation during deep cryogenic treatment, this transformation occurs with isothermal kinetics within the temperature range of −100 down to −170 °C with its largest intensity near −150 °C. No transformation is observed at −196 °C. The remarkable features of the isothermal martensitic transformation are: (i) the plastic deformation, which is explained by the absence of ageing of martensite at low temperatures; and (ii) the abnormally low tetragonality of martensite. In contrast to existing interpretations, the abnormally low c/a ratio is interpreted in terms of the capture of immobile carbon atoms by gliding dislocations during plastic deformation at low temperatures. A recommendation is proposed for optimizing the deep cryogenic treatment of tool steels.

Keywords: Tool steel; Martensitic transformation; Mössbauer spectroscopy; X-ray diffraction; Mechanical spectroscopy

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1. Introduction

In comparison with quenching at room temperature (RT) or temperatures not lower than −100 °C (conventional cryogenic treatment, CCT), the prolonged immersion of tool steels in liquid nitrogen or at least below −100 °C is usually denoted as a deep cryogenic treatment (DCT) (see e.g. [1,2]). The effect of CCT amounts to an increase in the hardness and a reduction in toughness, both due to the additional transformation of the retained austenite. In contrast, DCT increases the wear resistance and toughness, whereas hardness is not remarkably affected and even decreases.

In fact, DCT has been known for about a century, though attempts to clarify its physical meaning only started in the 1990s (e.g. [1–14]). A common point in the all available interpretations of the favourable DCT effect on the abrasive wear resistance is the denial of any role of martensitic transformation, which is based on the argument that this transformation is finished at temperatures higher than that of DCT. Such an approach ignores the existence of the isothermal martensitic transformation at low temperatures, which was first observed by Kurdyumov and Maximova [15].

One of the first hypotheses [3] attributed the effect of DCT to the precipitation of fine particles of η-carbide instead of the ε-carbide which usually precipitates during tempering of martensite quenched at RT or by CCT. It was also claimed (e.g. [4]) that DCT causes decomposition of martensite by precipitation of fine carbide particles

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during heating to RT. The idea of ultrafine precipitates of η-carbide (e.g. [5,6]) or even ε-carbide (e.g. [7]) as a reason for the improvement in mechanical properties due to DCT was reported in many subsequent publications, although at least two experimental facts are not consistent with it: (i) the η-carbide, first observed by Hirotsu and Nagakura [16], as well as the ε-carbide, are transient carbides and do not exist after tempering for secondary hardness (500–550 °C), which is a standard treatment for these tool steels; (ii) the η-carbide is precipitated in the high carbon martensite without any cryogenic treatment and, as shown by Taylor et al. [17], it is just an ordered ε-carbide where the occupation of corresponding sites by the carbon atoms causes a shift of metallic atoms, thus transforming the hexagonal crystal lattice into the orthorhombic one.

As a reason for the fine carbide structure after DCT, "low-temperature conditioning" is also discussed, the essence of which amounts to the diffusion of carbon atoms to dislocations and the formation of carbon clouds served as nuclei for subsequent precipitation during tempering (e.g. [1,5]).

However, the following data are at variance with this approach. First, the carbon atoms are essentially immobile at temperatures below −100 °C and cannot move towards dislocations or interfaces [18]. Second, the enthalpy of binding between carbon atoms and dislocations is about 0.8 eV (e.g. [19]), which is higher than the solution heat of transient carbides and even cementite. Therefore, the carbon clouds around dislocations cannot contribute to the precipitation of low-temperature carbides and even should delay cementite precipitation.

Some researchers have studied the effect of DCT on the substructure of martensite. An increase in dislocation density was reported by Popandopulo and Zhukova [20] based on X-ray diffraction (XRD) and electroresistivity measurements, although no corresponding experimental data were presented in that paper. Li et al. [9] observed an increase in the Snoek–Köster (S–K) relaxation strength after holding of the tool steel in liquid nitrogen in comparison with standard quenching at RT, and discussed this result as an evidence of a DCT-increased dislocation density. Generally, the S–K relaxation strength is proportional to the area swept by dislocations for one cycle of vibrations, and its increase can be due to a higher density of dislocations or an increase of their mobility (see e.g. [21]).

According to Molinari et al. [10], the substructure of martensite after DCT is characterized by the absence of twins, in contrast to the martensite quenched at RT where twins were observed. This unique observation correlates to some extent with data in Ref. [18] where the martensitic structure after DCT was characterized by a finer twinning in comparison with RT quenching.

A significant part of studies was devoted to a remarkable change in the size and distribution of carbide particles after DCT. Using scanning electron microscopy, Das et al. [11] identified two types of secondary carbides in the quenched CrMoV tool steel, small and large, both of them increased in their fraction with increasing time of holding in liquid nitrogen. These two types of precipitates were identified in Ref. [18] as vanadium-rich MC and M_2C carbides along with the eutectic carbide M_7C_3.

According to Mahmudi et al. [12], a significant refinement of carbides occurs in the tool steel M2 after DCT in comparison with CCT. Both steels were studied after tempering at 580 °C. Huang et al. [13] reported a more homogeneous distribution and a higher carbide volume fraction in the same steel after DCT.

A remarkable observation by means of optical microscopy was made by Gogte et al. [14], who reported a decrease in the size of the coarse carbides and an increased population of tertiary fine carbides up to the state of a "milky way" in high-speed steel T42 after DCT. This was interpreted by the authors as a precipitation of η-carbide in the course of DCT.

The aim of the present paper is to describe the isothermal martensitic transformation at temperatures below −100 °C as a physical mechanism responsible for improving the properties of tool steels by DCT.

2. Experimental

The tool steel X153CrMoV12 produced by powder metallurgy and containing (mass%) 1.55C, 11.90Cr, 0.70V, 0.86Mo, 0.38Si, 0.33Mn, 0.05N, 0.00S, 0.02P, 0.00Al was chosen for the studies. Due to the powder metallurgical technique, the given volume of eutectic carbides is finer and more evenly dispersed. Also, a smaller chemical segregation can be obtained in the solid solution. In some measurements the tool steel X220CrMoV13-4 produced by ingot metallurgy and containing (mass%) 2.2C, 13Cr, 4V, 1Mo was used. To ease the studies on low-temperature martensitic transformation, the reference steel X100Mn6 containing (mass%) 1.0 C and 6.0 Mn and free of undissolved carbides, was melted under protective argon atmosphere. This steel has a fully austenitic structure at RT, whereas the martensitic transformation proceeds at rather low temperatures and produces unaged virgin martensite.

The martensitic transformation was studied using dilatometry, Mössbauer spectroscopy, XRD and mechanical spectroscopy, i.e. internal friction (IF). In addition, a transmission electron microscopy (TEM) study of quenched samples after the low-temperature tempering was carried out in order to clarify the effect of the isothermal martensitic transformation on the precipitation of transient carbides.

Specimens $10 \times 10 \times 0.03\ \text{mm}^3$ for Mössbauer spectroscopy, $10 \times 10 \times 0.1\ \text{mm}^3$ for XRD diffraction and TEM, $0.7 \times 0.7 \times 60\ \text{mm}^3$ for IF were heat treated at 1080 °C under a protective argon atmosphere for 20 min followed by quenching at RT using an argon flow. In the case of dilatometric measurements, samples 6 mm in diameter and 10 mm long were heated in the dilatometer to 1080 °C, held for 20 min and cooled by gaseous nitrogen