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# Effect of copper addition on the characteristics of high-carbon and high-chromium steels



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### ABSTRACT

The effect of Cu addition on the microstructures and the tempering behavior of cold-work tool steels was investigated. 8% Cr steels with varying amount of Cu added from 0.22 to 2.56 wt% were prepared, then hardened by quenching and tempering. The alloys with different Cu contents showed similar fraction and size of  $M_7C_3$  carbide. Therefore, it could be known that the addition of Cu did not affect the formation of  $M_7C_3$  carbide which formed at high temperatures where Cu existed as a solute element. While increased Cu content reduced prior austenite grain size, the as-quenched hardness decreased due to higher hardness due to delayed softening, while after prolonged duration the softening rate was more diminished at the lowest Cu content. It was observed that Cu suppressed the formation of  $M_{23}C_6$  precipitate during tempering. Prior formation and coarsening of Cu precipitate could lead to enhanced tempering resistance in the early stages of tempering, whereas after prolonged duration, the effect was diminished due to the insufficient hardening caused by the suppressed precipitation of  $M_{23}C_6$ . By balanced co-precipitation of Cu and  $M_{23}C_6$  with refined grain size, the hardness and the impact toughness could be optimized at around 1 wt% of Cu addition.

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#### 1. Introduction

With the emerging needs for high fuel efficiency, many efforts have been devoted to the weight reduction of car body. One of them is the increasing application of high strength steels such as dual phase (DP) steel and transformation-induced plasticity (TRIP) steel to reduce the gauge thickness of structural parts and even outer panel.

As the strength level of steel sheet increases, additional difficulties are encountered in forming processes. A representative one is the increased load or contact pressure on tools and dies, which consequently leads to the early failures of them. Accelerated wear, chipping or cracking of tools and dies degrades the accuracy and reliability of forming processes, incurs additional costs. Currently, a large part of forming processes for making car body is cold forming processes such as cold stamping, trimming and piercing, although hot press forming technology is progressively adopted to produce very high-strength steel parts. In that sense,

the tool steels with improved properties will be critical for the active application of high strength steels as workpiece.

AISI D2 alloy has been widely used as a cold-work tool steel [1]. It has very high C and Cr contents of 1.4-1.6 and 11-12 wt%, respectively, along with some Mo addition of 0.7-1.2 wt% [1,2]. The high hardness obtained in tempered martensite with a large amount of hard carbide offers an excellent wear resistance. However, the toughness is very poor due to the presence of coarse primary carbides. It is generally observed that the fracture is induced from the cracked coarse carbides [3–5], whereas uniform distribution of fine carbides was reported to improve the toughness in uniaxial tensile deformation [6]. As a modification of D2, 8% Cr steel was developed. It has lower C and Cr contents of 0.8-1.0 and 7–8 wt% respectively compared to those of D2 steel [3,5,7], by which the steel benefits in toughness from the refined primary carbide [3,5]. The decrease of hardness due to lower C and Cr contents can be offset by increasing Mo or W addition as they effectively hinder the progress of softening during tempering, or they improve the tempering resistance. It was reported that 1.45% of additional Mo to 0.5C-0.5Mo base steel led to about 20% of hardness increase after tempering at around 500 °C [1].

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The improvement of tempering resistance should be important when the tempering is conducted at high temperature. Nowadays, hard coating such as chemical vapor deposition (CVD) or physical vapor deposition (PVD) is usually applied to the inserts in stamping dies to provide higher wear and galling resistance [1,8]. During these coating processes, the temperature of substrate material or tool steel is elevated. When the temperature exceeds the  $A_3$ temperature as in CVD, additional heat treatment and machining are needed due to the changes in mechanical property and dimension. Recently, application of various PVD techniques is considered because of the lower process temperature which generally ranges from 200 to 500 °C [8]. For the stabilization of microstructure and property during PVD, high-temperature tempering at about 500 °C is demanded. In this situation, delayed softening and enhanced secondary hardening by Mo and W addition [1] are more effective than to obtain high hardness in as-quenched condition to achieve required properties.

Cu in steel is known to increase the tempering resistance [9] at high temperature by the formation of ultrafine metallic Cu precipitate which can be observed by transmission electron microscopy [10,11] or atom probe tomography [12]. The strengthening by Cu precipitate should be smaller than that by carbides because it is softer and more deformable than ferrite or martensite matrix [13,14]. During deformation, both fine carbide and Cu particle can impede the movement of dislocation. When their size is identical below 70 nm, the dislocations are generally bowing out and bypass the carbides whereas Cu particles are sheared off by dislocation with smaller stress [14]. In spite of this, it is worth examining the effectiveness of Cu precipitate on tempering resistance for the sake of cost effective alloy design because the elements which are added to generate the secondary hardening such as Mo, W and Co are expensive. However, there have been little informative works on the effect of Cu in high-C steels such as cold-work tool steels [12,13], even concerning the general characteristics in the evolution of microstructure. Therefore, in this study, for the 8% Cr steel with various Cu levels, the effect of Cu on the microstructures and on the tempering response is investigated including possible interaction of Cu with the formation of carbides.

#### 2. Experimental

The chemical composition of investigated alloys is listed in Table 1. They are 8% Cr steels with Cu additions of 0.21, 0.98, 1.63 and 2.56 wt%, which are denoted as A0, A1, A2 and A3, respectively. The square bar ingots were reheated to 1200 °C and held for 1 h, then hot-forged to reduce the initial cross section of  $100 \times 100 \text{ mm}^2$  into  $50 \times 50 \text{ mm}^2$ . The forged bars were annealed at 870 °C for 4 h, then slowly cooled in the furnace to obtain the microstructure consisting of ferrite with spheroidized carbides. From the annealed bars, specimens with dimension of  $12 \times 12 \times 60 \text{ mm}^3$  were machined for heat-treatment and subsequent mechanical tests. The quenching and tempering heat treatment was carried out using a tube-type furnace. For quenching, the specimens were austenitized at 1030 °C for 30 min in Ar atmosphere and then air-cooled. They were tempered at 520 °C

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Chemical	compositions	of the	alloys	(wt%).

Alloy	С	Si	Mn	Cr	<sup>a</sup> Mo <sub>eq</sub>	Cu
A0	1.05	0.97	0.41	8.18	1.82	0.22
A1	1.00	0.94	0.42	8.16	1.72	0.98
A2	1.07	0.92	0.41	8.06	1.76	1.63
A3	1.06	1.04	0.45	7.96	1.73	2.56

<sup>a</sup> Mo<sub>eq</sub>=[wt% Mo]+0.5[wt% W].

for 1–4 h followed by air-cooling to room temperature and the same tempering cycle was repeated. In industrial practice for the tempering of tool steels, tempering is generally repeated twice or more in order to extend the decomposition of retained austenite by cooling and to stabilize the fresh martensite and carbide formed on tempering [1]. In Fig. 1, this quenching and tempering heat treatment is shown schematically. It is noted that only the tempering duration in the single cycle is presented in the remaining part of this paper instead of the total duration.

Vickers hardness was measured on the cross section of the bar specimens with 10 Kg load. The hardness test was performed on both as-quenched (denoted as Q) and quench-and-tempered (denoted as QT) specimens. The impact toughness was evaluated by the Charpy impact test after additional machining of the specimen to remove the decarburized layer on the surface and the detailed dimension of the specimen is presented in Fig. 2. Because of limited amount of specimen, the impact toughness was measured only for QT specimens as the impact toughness just after quenching attracts little industrial interest. For convenience, the specimens were designated with the alloy name followed by heat treatment condition. For example, the as-quenched specimen of the alloy containing 0.98 wt% Cu was named as A1Q, and after tempering for 2 h as A1QT2. The full list of the specimen designations is presented in Table 2.

For microscopic characterization using optical microscope (OM) and scanning electron microscope (SEM), the cross sections of the samples were mechanically polished and etched with a solution of 95 ml ethanol, 5 ml hydrochloric acid and 1 g of picric acid (Villela's reagent). The inverted type metallographic OM, Epiphot 300 by Nikon and the field emission (FE) type SEM, JSM-7001F by JEOL were used. Secondary electron images (SEI) from the SEM operating at 5 kV were used to evaluate the prior austenite grain size in Q specimens; and the volume fraction and average size of M<sub>7</sub>C<sub>3</sub> carbide in QT2 specimens were subjected to tempering for 2 h. The detailed procedure for this carbide analysis is described in the following section. For the detailed analysis of fine precipitates which are evolved during tempering, the field emission type transmission electron microscope (TEM), JEM-2100F by JEOL was used. Thin foil samples were prepared using twin jet polisher in a solution of 750 ml methanol and 250 ml nitric acid at 15 °C, and the TEM was operated at 200 kV. The high power X-ray



Fig. 1. Schematic diagram of the quenching and tempering heat treatment.



Fig. 2. Specimen for C-notched Charpy impact test.

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