An Explanation of Possible Damascus Steel Manufacturing Based on Duration of Transient Nucleate Boiling Process

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Abstract: - In the paper the new explanation in manufacturing of Damascus steel, based on discovered the specific characteristics of transient nucleate boiling processes, is provided. According to discovered characteristics, duration of transient nucleate boiling process is directly proportional to squared size of a body and inverse proportional to thermal diffusivity of a material, depends on configuration of a body, thermal properties of liquid and initial temperature of a body. The surface temperature of a body during transient nucleate boiling process maintains at the level of boiling point of liquid and cannot be below it. Based on these characteristics, the new hypothesis regarding manufacturing of Damascus steel is proposed according to which the melted high carbon steel (containing 1 – 2% carbon) was casted into copper forms cooled by cold water and then the steel was many times forged and quenched in special water salt solutions until finishing transient nucleate boiling process. Such simple technology provided extremely small spherical carbides distributed in steel which acted as a saw and made steel very strong.

Key – Words: - Transient nucleate boiling process, Damascus steel, Hammering, HTMT and LTMT processes, Highly strengthened plain carbon steels.

1 Introduction

Damascus steel was a hot - forged steel which was used in Middle East's sword making from 1000 to 1700 A.D. [1-5]. The foundation for Damascus steel was "wootz" steel which originated in India, Sri Lanka and later spread to Persia [4 - 7]. Steel making sites were found in Sri Lanka that made high carbon steel as early as 300 B.C. According to Ref. [8], the small spherical grains of cementite microstructure were also found in the archeological items from Pol'tse, a settlement at Amur river, V-IV century B.C. Raw materials and Damascus steel crafting instruction are not longer available. Details of technology, which was used by the capable metallurgists from Pol'tse, is not known [8]. The ancient technique reached modern - day Turkmenistan and Uzbekistan around 900 A.D., and then the Middle East circa 1000 A.D. There are numerous publications where this matter is widely discussed [9 - 16]. It is underlined that India has been reputed for its iron and steel since ancient times, the time of Alexander the Great (356 B.C. - 323 B.C.)[5] . When Alexander the Great got to India he ordered to be delivered to him “100 talents of Indian steel” [5]. Studies on “wootz” indicate that is was an ultra - high carbon steel with 1 - 2% carbon. Metal smiths in India and Sri Lanka developed a technique that produced unusually high purity “wootz” steel. Glass was added to a mixture of iron and charcoal and then heated. The glass would act as a flux and bind to other impurities in the mixture, allowing them to rise to the surface and leave a pure steel when the mixture cooled. It is interesting to know that more than two millennium ago ancient metallurgists manufactured pure ultra - high carbon steel which was of high quality [4, 5]. Later the main features of the method of ancient metallurgists were rediscovered by Anosov in his systematic research at Zlatoust Arms Factory in Russia during 1828 - 1840 [1, 2]. The essence of the Anosov's method consists in many cycles of forging the ultra - high carbon steel at high temperature with intermediate annealing. Accurate microstructure studies of Damascus steel with correct explanation of its strengthening due to formation of fine spheroidized carbides were published by N.T.Belaiew in Journal of the Iron and Steel Institute [3]. Microstructure of a typical Damascus sword is characterized by formation of spherical cementite particles of 5 - 20 μm [3, 8].

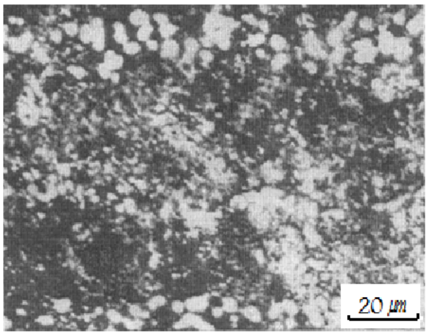


Fig. 1 Microstructure of Damascus sword [8].

Fundamental scientific research on the development of high-carbon steel with the uniform submicron-size cementite structure was performed by Sherby in the 1970s and 1980s. The Sherby method for forming high-carbon steel closely resembles the method of Damascus craftsmen. Both methods include numerous cycles of intensive high temperature deformation and annealing. While Damascus steel was formed by forging, the Sherby method utilized rolling as the deformation means. Several U.S. Patents of Sherby describe an ultra high-carbon steel having a carbon about 1.0% - 2.3 % and an iron grain matrix with uniformly dispersed cementite [14, 15, 16]. The iron grains in the steel were no greater than 10 microns with spherical carbides [9 - 13]. Unfortunately, contemporary methods of manufacturing Damascus steel are rather complicated and expensive; that is why they are not widely used in practice. To decrease cost of technology, author [8] proposed to cast high – carbon steel in preheated to 700°C casting forms which provide optimal cooling rate for getting spherical small carbides (0.1 - 5 μm) and enough strengthened ultra – high carbon steel (1200 – 2500 MPa with 10% of plasticity) without further thermomechanical treatment, quenching and annealing. However, casting into preheated form doesn't allow achieving very small particles of carbides without thermomechanical treatment and quenching. A team of researches based on Technical University of Dresden used x - rays and electron microscopy to examine Damascus steel. They discovered the presence of cementite nanowires and carbon nanotubes in ancient Damascus steel [17, 18]. It is believed that these nanostructures are as a result of the intensive forging [17, 18].

2 Governing equations of the process of precipitation

Below are equations describing the two mechanisms of precipitation hardening. Dislocations cutting through the small carbides [19]:

$$\sigma_\tau = \frac{r\gamma\pi}{bL} \tag{1}$$

where σ_τ is material strength, *r* is the second phase particle radius, γ is the surface energy, *b* is the magnitude of the Burgers vector, and *L* is the spacing between pinning points. This governing equation shows that the strength is proportional to *r*. This means that it is easier for dislocations to cut through a material with the smaller second phase particles. As the size of the second phase particles increases, the particles impede dislocation movement and it is very difficult for dislocations to cut through the material. It means that the strength of a material increases with increasing r.

Dislocations bowing around the particles is described by Eq. (2) [19]:

$$\sigma_\tau = \frac{Gb}{L-2r} , \tag{2}$$

where *G* is the shear modulus. This governing equation shows that for dislocation bowing the strength is inversely proportional to the second phase particle radius r and distance between particles L. Dislocation bowing is easily occurred when there are large particles presence in the material.

Considered governing equations show that the precipitation hardening mechanism depends on the size of the precipitate particles. At small r cutting dominates, while at large r bowing dominates.

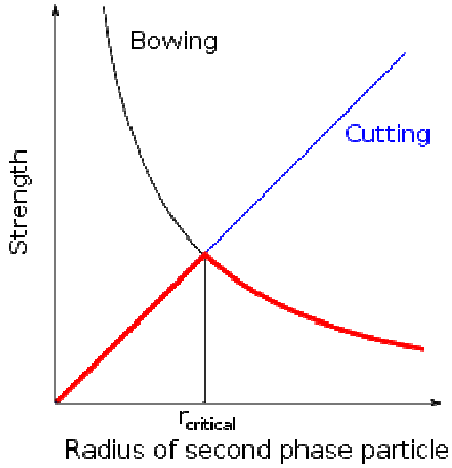


Fig. 2 Strength of steel versus radius of second phase particle [19].

That is why a critical radius, at which max strengthening occurs, can be evaluated [19]. This critical radius is within 5-30 nm or 0.005 - 0.03 μm [19]. Provided calculations show that spherical carbides of 0.1 – 5 μm are almost 1000 times larger as compared with the critical radius of carbides; and they cannot cause extremely high strength of steel. Authors [20] achieved nanoparticles by cooling intensively melted metal with cold water using special technology.

3 Intensive cooling of melted UHCS to receive suitable particles of carbides

To obtain very small particles, cooling rate of melted steel should be very high (see Eq. 3) [21].

$$r_{cr} = \frac{2\sigma}{\Delta f_V}. \qquad (3)$$

Here σ is surface tension; Δf_V is difference of free energy for one unit of volume between initial phase and supercooled phase. The higher cooling rate, the smaller size of particles to be precipitated. However, during intensive quenching transformation austenite into martensite should be prevented to escape crack formation and big distortion of the castings. It can be easily done by using very simple technique shown in Fig. 3 which is governed by main laws of nucleate boiling processes (Eq. (4) and Eq. (5)).

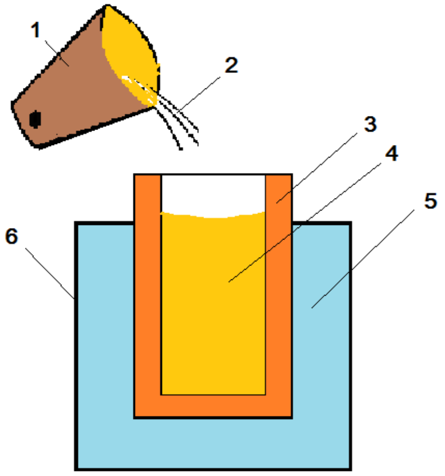


Fig. 3 Possible way of casting might have been used by ancient metallurgists: 1 is ladle; 2 is liquid metal; 3 is water – cooled copper form; 4 is solidified metal; 5 is water (quenchant); 6 is tank with water.

Using Eq. (4) and Eq. (5), one can produce very high cooling rate and eliminate transformation of austenite into martensite. For this purpose the casting form is cooled by water or any suitable liquid quenchant. During casting water starts to boil and duration of boiling can be evaluated from Eq. (4). At the end of transient nucleate boiling process water in tank will be almost 100°C. Since for UHCS martensite start temperature Ms is 100°C and below, no martensite transformation will occur (see Fig. 4). So, Eq. (4) helps to evaluate duration of transient nucleate boiling process [22], *i.e.*

$$\tau_{nb} = \overline{\Omega} k_F k_W \frac{D^2}{a}, \qquad (4)$$

where value $\overline{\Omega}$ depends on initial temperature and condition of cooling. Coefficient k_F depends on configuration of castings. For plate-shaped forms k_F = 0.1013; for cylinder – shaped form k_F = 0.0432; for spherical – shaped forms k_F = 0.0253; k_W is dimensionless coefficient which depends on liquid flow velocity. For motionless liquid $k_W = 1$. For high flow velocity of liquid which prevents nucleate boiling $k_W = 0$. That is why for different condition we have $0 \le k_W \le 1$. *D* is thickness of the body: diameter of cylinder, sphere or thickness of the plate; *a* is thermal diffusivity of material. The character of surface temperature changing during transient nucleate boiling (self- regulated thermal process) is shown in Fig, 5 (see curve 2). Such trend can be written as [22]:

$$\overline{T}_{sf} = T_S + \overline{\xi}_0 \approx const, \qquad (5)$$

where $\overline{T}_{sf}$ is average surface temperature of a body; T_S is saturation temperature; $\overline{\xi}_0 = \overline{T}_{sf} - T_S$ is average wall overheat.

Very fast cooling can cause martensite transformation which will results in crack formation (see curve 1 in Fig. 5).

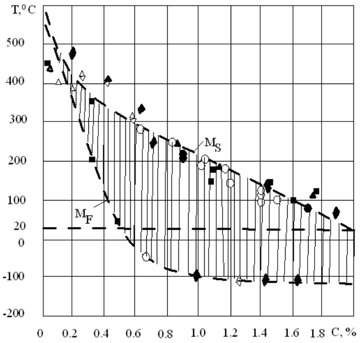


Fig.4 Martensite start temperature M_S and martensite finish temperature M_F versus content of carbon in steel.

4 High temperature and low temperature thermomechanical treatment

For ultra – high carbon steel (UHCS) martensite start temperature is equal to 100°C and less (see Fig. 4); and it means that during transient nucleate boiling process transformation of austenite into martensite will be delayed for enough long time which can be calculated by Eq. (4). During this time low temperature thermomechanical treatment (LTMT) can be easily fulfilled for for high carbon steel and UHCS. It cannot be done when quenching high carbon steel and UHCS in oil. Only alloy steels can be used for LTMT processing. Discovered characteristics (see (Eq.(4) and Eq. (5)) make LTMT possible and this process is effective for plain carbon steels including high carbon steel and UHCS. There is a great probability that ancient metallurgists might have used some empirical data connected with the boiling processes. It could be cooper melting form immersed into cold water (see Fig. 3) which heated cold water to boiling point and then UHCS was heated to high temperature and many times forged. Low temperature and high temperature thermomechanical treatment possibly was used.

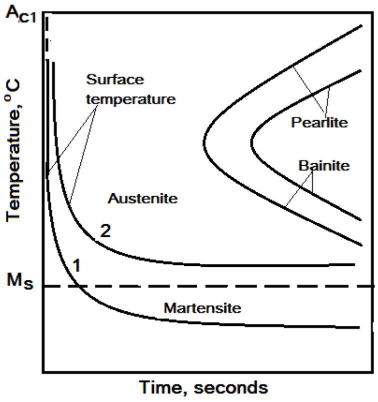


Fig. 5 Surface temperature versus time during transient nucleate boiling (self - regulated thermal process): 1 is conventional process; 2 is intensive cooling process which delays transformation austenite into martensite.

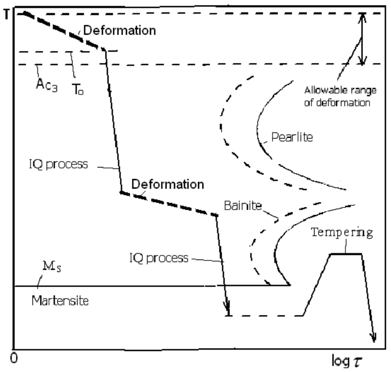
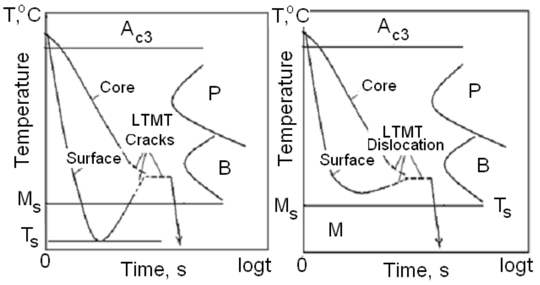


Fig. 6 The scheme of low and high temperature thermo mechanical heat treatment [21].

The scheme of high temperature and low temperature thermomechanical treatment is shown in Fig. 6; and incorrect low temperature thermomechanical treatment (LTMT) (a) and correct LTMT (b) are shown in Fig. 7. So, discovered characteristics of transient nucleate boiling processes can introduce very simple way of achieving nanoparticles of carbides to strengthen plain carbon steels including UHCS.



a) b)

Fig. 7 Scheme of incorrect (a) and correct (b) low temperature thermomechanical treatment (LTMT) [21].

5 Discussion

It has been fulfilled numerous investigations worldwide and written numerous books and articles since 1841 concerning the process of Damascus steel manufacturing. Due to these investigations, it has been established that Damascus steel is ultra – high carbon steel containing spherical small carbides (5 – 20 μm). These small carbides create chains (see Fig. 1) which are visible clearly as a macrostructure (Fig. 8).

Fig. 8 Close-up of a 16th century Damascus steel sword [5].

Calculations show that optimal size of carbides should be at least 100 times less to provide high strength of material. Fig. 1 shows that along with small carbides could be invisible carbides. Authors [19, 20] observed even nanotubes which must have been as a result of intense hammering. It should be underlined that it is impossible to manufacture Damascus steel just cooling melted UHCS in preheated to 700°C casting form or copper form. This process will provide raw material which should be many times hammered and quenched to receive high strengthened material like Damascus steel. The new characteristics of transient nucleate boiling process have been discovered by author [22] which can be used to manufacture high strength materials on the basis of plain carbon steels including UHCS.

6 Conclusion

1. The possible technology of Damascus steel manufacturing is explained on the basis of discovered specific characteristics of transient nucleate boiling processes [22].
2. A method for achieving high cooling rate of melted high carbon steel and UHCS is proposed, which can eliminate martensite transformation and provide formation of nanoparticles of carbides in steel.

3. It is impossible to achieve nanoparticles by casting high carbon steel or UHCS into copper or preheated to 700°C forms [23, 24] without their intensive cooling.

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