J Mater Sci (2009) 44:2192–2197
DOI 10.1007/s10853-008-3007-1

FESTSCHRIFT IN HONOUR OF PROF T R ANANTHARAMAN ON THE OCCASION OF HIS 80TH BIRTHDAY

Correlation between microstructure and phosphorus segregation in a hypereutectoid Wootz steel

M. R. Barnett · R. Balasubramaniam ·
Vinod Kumar · Colin MacRae

Received: 16 May 2008 / Accepted: 16 September 2008 / Published online: 11 October 2008

Abstract The influence of bands rich in phosphorus on the microstructure of hypereutectoid Wootz steel implement is described. Electron probe micro-analysis is combined with optical microscopy. Phosphorus-rich bands are seen to correspond to regions of internal cracking, carbon depletion, and enhanced frequency of spheroidized cementite in place of pearlite. A rationale for the findings is presented in terms of the influence of phosphorus on the Fe–C phase diagram and on the rate of the eutectoid reaction.

Introduction

Wootz is a high carbon hypereutectoid steel that originated from the south of India and was historically quite popular [1]. The name of this material is a corruption of the term used to indicate “melt” in several languages of south India [2]. There is a saga surrounding this material in terms of its extraction, means of manufacture and purported extraordinary properties, and this can be followed in a number of places [3–5].

Wootz steels were popular because of their ability to be forged into tough cutting objects (like swords, blades, axes) and protective armor [6]. The starting point for the processing was an ingot manufactured using a unique furnace and a specially designed crucible. The carbon content in these steels is typically about 1.1–1.8 wt% and therefore the typical cast structure can be expected to consist of proeutectoid cementite with a pearlite matrix along with some Widmanstätten cementite. The resultant material is brittle. However, when forged the structure can display considerable toughness. Such processing was not trivial and attempts to understand the method of forging played an important role in the development of the modern study of physical metallurgy [7]. Like ancient Wootz, modern ultra high carbon (UHC) steels rely on the conversion of the brittle cast structure to a tough product characterized by spheroidized cementite in a ferritic matrix. This is achieved using thermomechanical processing [8] and appropriate alloying additions (e.g. Al) [9].

The quality of ancient steel cutting objects was often determined by the “watering” pattern evident on the blade surface after suitable surface treatment. These “watering” patterns result from the alignment of coarse cementite in bands. The origin of the banding has been the subject of intense debate. Taleff et al. [10] have attributed the banding to mechanical “pancaking” of proeutectoid cementite. Verhoeven et al. [4] have pointed to the important role played by the segregation of impurity elements, notably vanadium. In the segregated regions, coarse cementite particles congregate. The separate stands of these two groups can be appreciated in their recent communications [11, 12]. Despite the debate, it is not impossible that both effects are quite important [13, 14].

Although the more recent work by Verhoeven et al. [5, 11] has emphasized the role of carbide-forming elements, it

---

M. R. Barnett (✉)
Centre for Material and Fibre Innovation, Deakin University,
Geelong, Australia
e-mail: barnettm@deakin.edu.au

R. Balasubramaniam · V. Kumar
Department of Materials and Metallurgical Engineering,
Indian Institute of Technology, Kanpur 208 016, India

C. MacRae
Microbeam Laboratory, CSIRO Minerals, Bayview Avenue,
Clayton, Australia

is important to note that phosphorus is a ubiquitous constituent of Wootz steels at levels of the order of 0.1% by weight [4]. In some instances, phosphorus segregation at these levels can account for coarse carbide banding [5]. The origin of the phosphorus is not entirely clear. Traditionally, Wootz steel was melted in closed crucibles and the charge was wrought iron along with carbon in the form of charcoal (South Indian process) or mixture of wrought iron and cast iron (Hyderabad process) [15]. The Wootz steel smiths were particular in adding certain kinds of barks and leaves of plants in the Wootz steel crucible before it was sealed and fired in furnaces. It was pointed out by Heath [16] that the leaves would have provided additional hydrocarbons which would have made the processing time shorter. It appears that the shrub *Cassia auriculata* was often employed [17]. This particular plant removes phosphorus from the ground and a higher concentration is collected in the bark of the shrub. It is possible that the origin of at least some of the phosphorus in the Wootz was through the intentional addition of *C. auriculata*.

In the case of *hypoeutectoid* steels, it is well known that microsegregation of phosphorus into the dendritic regions can be responsible for ferrite banding [18–20]. This arises chiefly from two sources [21]. One is due to the redistribution of carbon that occurs while the material is austenitized and which arises from the effect of phosphorus on carbon activity. Phosphorus raises the activity of carbon so that phosphorus regions tend to become depleted in carbon. The second origin is held to be the impact phosphorus has on the transformation temperatures upon cooling. Phosphorus increases the Ar_3 temperature so that ferrite forms first in these areas. A ferrite band then tends to form in the region of high phosphorus gradient at the band edge as ejected carbon is received by the neighboring low phosphorus regions.

The present short communication presents some microstructural observations of a wedge-shaped *hypereutectoid* Wootz implement [22]. Such implements have received little attention in the literature and are of interest because they display a range of forging strains. The work points out that phosphorus banding can also have a significant impact on the nature of the finer eutectoid cementite.

Experimental

The tool that was used in the present study was obtained from a blacksmith named Mandaloji Gangaram from the village of Konapuram, located in Kammarpalli Mandal of Nizamabad district of Northern Telangana region in Andhra Pradesh state in India. This was collected and recorded during the recent survey of Wootz steel-making sites in Medieval Telengana [23]. This village is in very close proximity (15 km) to the famous Wootz-producing center of Konasamudram [24].

Fig. 1 Overall view of the implement that was used in the present study

The overall view of the object is shown in Fig. 1. The left end of the tool was almost square. The tool has been progressively reduced in thickness until it was flat (with a sharp tip) at one end, resulting in a visible taper. The sample was prepared for investigation by cutting it in half along the length [22]. From one of the halves, smaller samples were sectioned in order to observe the microstructures. The present study is concerned mainly with the region of intermediate strain in the middle of the sample.

First, the chemical composition of the sample was measured from a region 3.5 mm from the rear end of the blade by glow discharge optical emission spectrometry (GDOES) using a Leco GDS 850A equipment. The trace element composition is (in wt%): 1.8% C, 0.006% Mn, 0.061% Si, 0.009% S, 0.14% P, 0.002% Mo, 0.001% Nb, 0.11% Cu, 0.017% Zr, and 0.046% Ce. The composition is fairly typical of a Wootz steel object [4].

The sectioned samples were mounted and polished with 240, 400, 900, and 1200 grit silicon carbide papers, followed by polishing with diamond paste of 15, 9, 6, 3, and 1 μm sizes. They were finally washed with distilled water and ultrasonically cleaned in ethanol. The microstructures were revealed after etching in 2% Nital for 5–10 s. The microstructures were studied in a high-resolution optical microscope (Nikon Eclipse 80i) and scanning electron microscope (SEM LEICA S440). Local compositions were obtained in an FEG electron probe microanalyser (EPMA), model JEOL 8500F, equipped with five wavelength dispersive and two energy dispersive spectrometers. Two phosphorus maps were collected using the phosphorus Kα line. The first map area was selected to investigate the possible role of this element in a region of local voiding/cracking. This map was collected with an accelerating voltage of 15 kV, a beam current of 100 nA, a pixel size of 2 μm step, across an area of 2000 × 2000 μm. The second map was collected across a number of bands of alternating cementite morphology. Since the microstructure in this region was finer, the accelerating voltage was lowered to 12 kV to improve the spatial resolution. The step size was reduced to accommodate the increased resolution. The beam conditions were 12 kV, 100 nA beam current, 300 nm pixel size and an area of 300 × 1200 μm was mapped. Maps were collected by stepping the stage with a stationary focused beam.

The maps were processed using commercial software which allows semi-quantitative *k*-ratio maps of phosphorus and carbon to be generated. The *k*-ratio is given by the following expression:

$$k\text{-ratio} = C_0(I/I_0) \quad (1)$$

where C_0 is the concentration of a given element in a standard and I and I_0 are the specimen and standard intensities, respectively, corrected for instrumental effects. The *k*-ratio scales with the concentration of the element of interest. A full quantitative analysis requires careful background measurements and corrections that were deemed to be unnecessary for the present purposes.

Results

Observation of the macrostructure by eye revealed the presence of a decarburized region on the surface at the large (least deformed) end of the implement. This decarburized zone is most likely to have formed during preheating of the ingot prior to forging. It may well have been intentional to produce such a "case" on the material to improve its ability to be forged [25].

The arrangement of the coarse cementite particles in the low strain region (Fig. 2a) does not correspond to any alignment that can be expected to occur from the deformation and therefore probably reflects that produced during the initial cooling of the ingot. These coarse cementite particles may well follow the austenite inter-dendritic regions or coarse Widmanstätten cementite such as that seen in Ref. [26]. In addition to the coarse cementite particles, the low strain microstructure also consists of pearlite, grain boundary cementite and a few examples of relatively fine Widmanstätten cementite. In the intermediate strain region (Fig. 2b), breaking up of the grain boundary cementite can be noted. There is also a distinct banded structure evident in this region when viewed at lower magnifications (Fig. 2c). The high strain region shown in Fig. 2d displays relatively fine spheroidized cementite.

There are two notable features that were detected in the intermediate strain region. First, some regions exhibit significant microcracking. In order to test the hypothesis that phosphorus was involved in the cracking, FEG-EPMA mapping was performed. The maps show that the cracked region contained higher phosphorus levels, Fig. 3 (i.e. the matrix in the area of cracking is a lighter shade than in the adjacent uncracked area). Interestingly, in the high strain region of the implement, no cracks were observed and it can be surmised that they were closed in this region by continued forging. Secondly, periodic phosphorous banding is evident (Fig. 4). As in Fig. 3, the lighter areas in the image indicate increased phosphorus levels. The microstructures seen in and between the bands are provided in

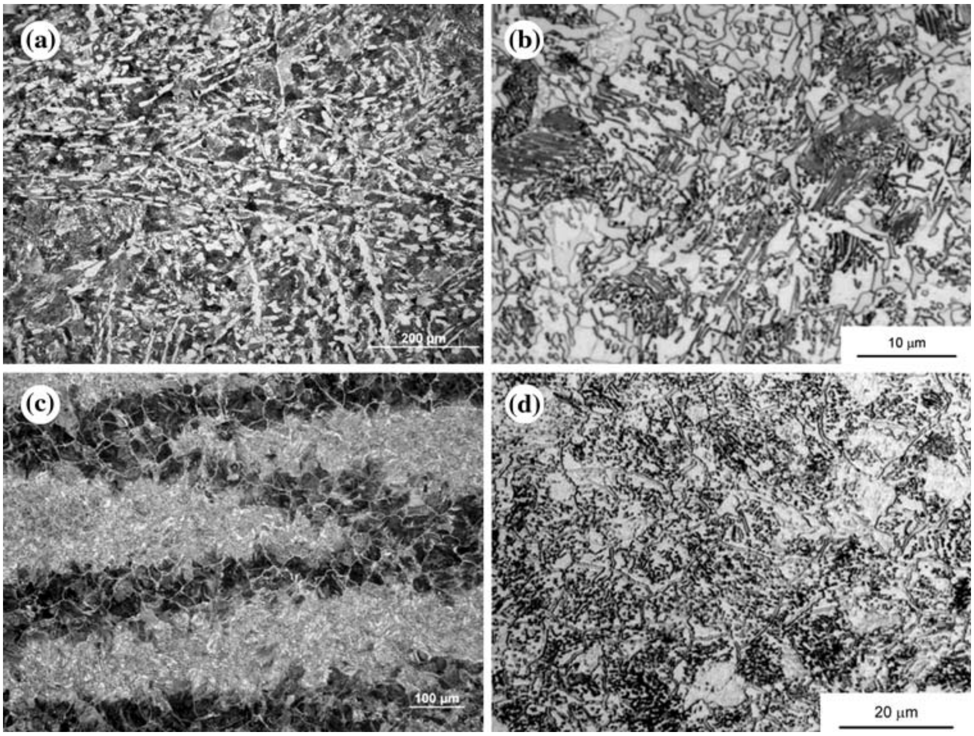

Fig. 2 Optical microstructures from three different regions of the worked object **a** low strain region, **b** intermediate strain region, and **c** banding evident at lower magnifications in the intermediate strain region and **d** high strain region (tip). Direction of elongation during forging is horizontal in all images throughout

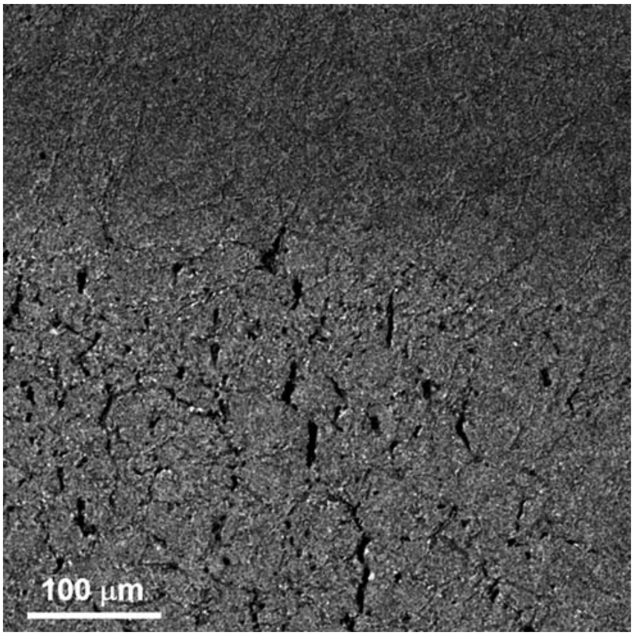

Fig. 3 Electron probe microanalysis map of a section of the intermediate strain region where cracks were noted. Shading is according to the intensity of the phosphorus Kα peak ratio in the range of 0.2–0.9, where *white* corresponds to the higher phosphorus levels

Fig. 5 in terms of carbon level maps. This reveals the cementite morphologies. There is clearly less pearlite and more fine (eutectoid) spheroidized cementite in the regions high in phosphorus. Thus it is possible that phosphorus promotes the formation of spheroid-shaped eutectoid cementite.

Discussion

The cracking seen in some of the phosphorus-rich bands is most likely due to the presence during forging of small amounts of the ternary eutectic, steadite. Formation of this phase has been observed in phosphorus-rich regions of a material with similar levels of carbon, phosphorus, and sulfur to the present [26]. The melting point of steadite is relatively low (between 939 °C [26] and 950 °C [27]). It is quite likely that this temperature was exceeded at some stage during forging and localized melting produced hot shortness and associated cracking. The small bright high phosphorus regions evident in Fig. 3 may be locations of remnant Fe_3P from the steadite [26].

Turning to the banded structures observed in the present material, it is interesting to note the band morphology evident in Fig. 2c takes an appearance more readily linked to a prior grain boundary network than a dendritic structure. But an origin in a coarse primary dendrite structure cannot be discounted. The latter is certainly a far more likely location for phosphorus to accumulate during solidification. Irrespective of its initial microstructural origin, there is evidence for the redistribution of carbon

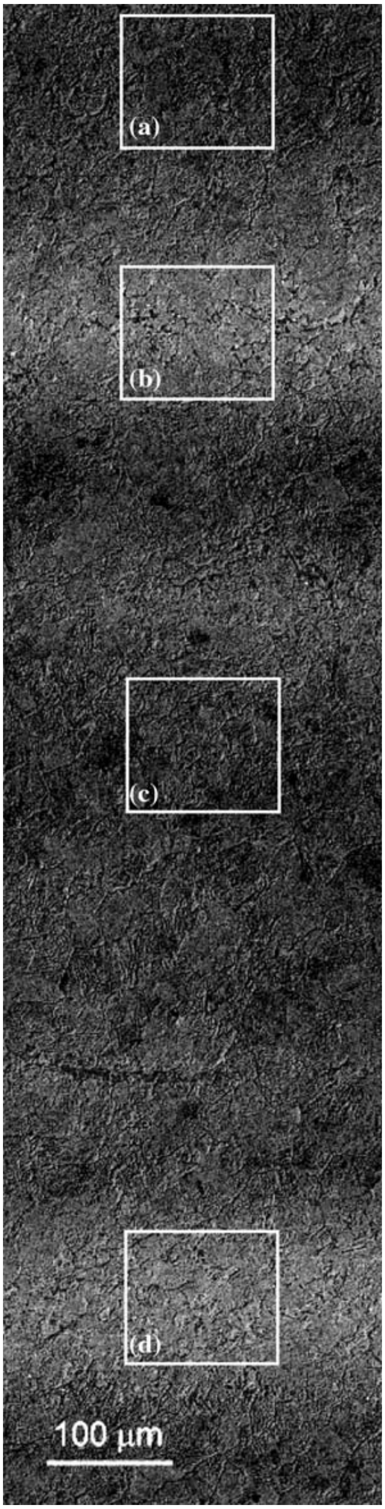

Fig. 4 Electron probe microanalysis map showing phosphorus banding: *light shading* indicates higher phosphorus levels as per Fig. 3. The *boxed regions* are enlarged in Fig. 5

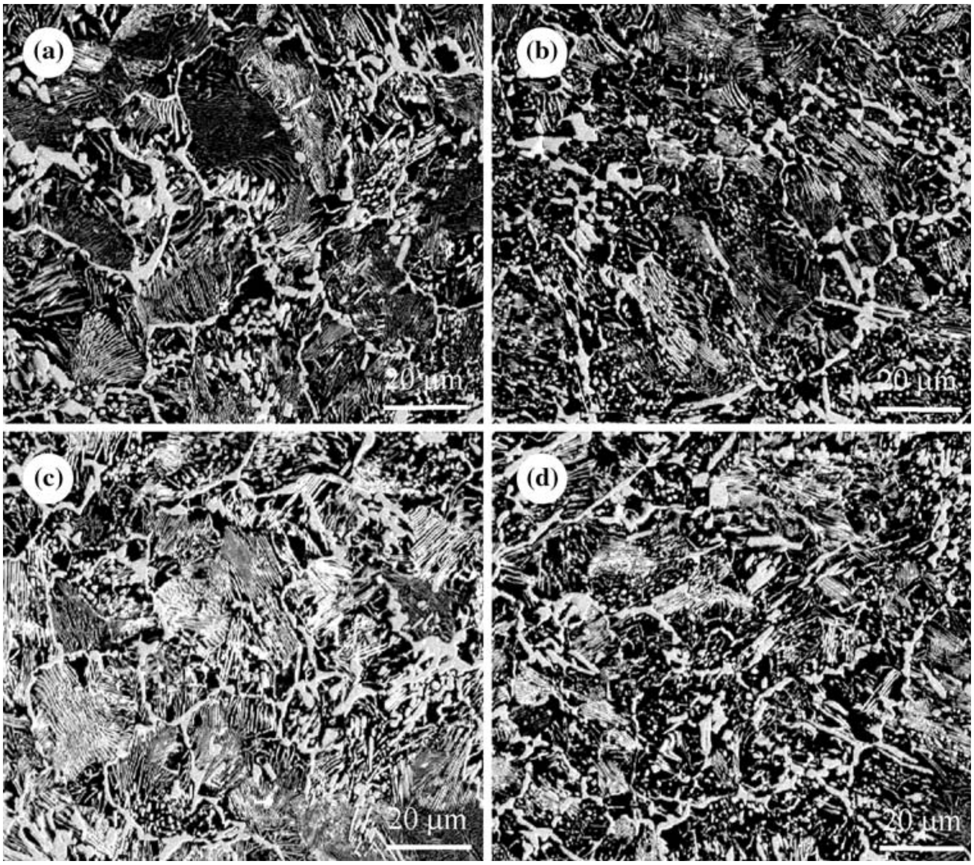

Fig. 5 Electron probe microanalysis maps corresponding to the *boxed regions* in Fig. 4 showing carbon levels (*light shading* indicates higher carbon levels—the *k*-ratio ranges from 0.2 to 4.0 over the grey scale plotted). Maps (**b**) and (**d**) correspond to high phosphorus levels and these show more spheroidized cementite and less pearlite than the low phosphorus regions (**a**) and (**c**)

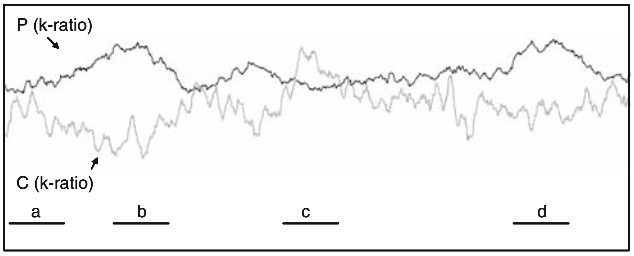

Fig. 6 Plot of relative carbon and phosphorus levels (based on *k*-ratios) obtained from averaging over the *horizontal direction* in Fig. 4. The left of the plot corresponds to the top of Fig. 4 and the sections of the trace corresponding to the *boxed regions* in Fig. 4 are shown for reference. An inverse relationship between carbon and phosphorus is evident

from the phosphorus-rich bands into the neighboring phosphorus-poor material. This is shown in Fig. 6. As mentioned earlier, such an effect can be understood in terms of the impact phosphorus has on carbon activity. It can also be thought of in terms of the tendency for phosphorus to take carbon sites in the austenite lattice [28]. For equilibrium conditions, the phosphorus-rich bands will tend to display less cementite following austenitization prior to forging. However, equilibrium conditions are unlikely to prevail during the many forging and reheat cycles employed in blade manufacture (e.g. [5]). This is particularly true given that the latter stages forging at least were probably carried out at the low temperatures of ~750–850 °C [26].

Given that low austenitization temperatures are typical in Wootz forging, it is expected that the probability of finding a “divorced” or spheroidal eutectoid cementite structure would be high [29]. Such structures are favored at low austenitizing temperatures because under these conditions the likelihood of retaining a fine dispersion of undissolved cementite is high. Upon cooling below A_1, this dispersion can coarsen with the progress of ferrite growth fronts without the formation of a typical pearlitic structure. Such an occurrence will obviously be more likely for austenitization that has not progressed to equilibrium, in which higher levels of cementite can be expected.

It appears that the phosphorus may be slowing the dissolution of cementite during the austenitization reheating steps that occur throughout the forging process. Certainly a “solute drag” effect of phosphorus has been observed in pearlite formation [30] but no explicit study has been located by the authors on the role of phosphorus on cementite dissolution. The phosphorus can be expected to be segregated to the cementite–austenite interfaces [31] and to resist the expulsion of carbon into the surrounding austenite due to the effect of phosphorus on C activity described earlier. It is thus tentatively speculated that slowed cementite dissolution in the phosphorus-rich bands is the most likely cause of the higher degree of spheroidal eutectoid cementite seen in these bands. The retained cementite can be expected to act as nuclei upon cooling through the eutectoid temperature and to produce spheroidized cementite rather than pearlite.

Conclusion

The presence of phosphorus-rich bands in Wootz steel leads to local cracking, bands of altered cementite morphology (more spheroidized than pearlitic), and inverse carbon segregation. The effect of phosphorus on cementite morphology can be understood best in terms of a solute drag exerted by the tendency of phosphorus to slow the rate of cementite decomposition. The phosphorus-rich bands will tend to contain more non-equilibrium cementite in the austenite that can act as sites for the growth of spheroidized cementite through the eutectoid reaction.

Acknowledgements The authors acknowledge the kind contribution of Dr. S. Jaikishan, Reader in History, SNLSA Degree College, Dharmapuri, Karimnagar District, for providing the sample used in this study. The financial support extended to V.K. for his stay at Deakin University by Deakin University is appreciated.

References

1. Smith CS (1965) A history of metallography—the development of ideas on the structure of metals before 1890. The University of Chicago Press, Chicago
2. Srinivasan S, Ranganathan S (2004) India's legendary Wootz steel: an advanced material of the ancient world. Tata Steel, Jamshedpur
3. Wadsworth J, Sherby OD (1980) Prog Mater Sci 25:36. doi:10.1016/0079-6425(80)90014-6
4. Verhoeven JD, Pendray AH, Dauksch WE (1998) JOM 50(9):58. doi:10.1007/s11837-998-0419-y
5. Verhoeven JD (2002) Steel Res 73:356
6. Balasbramaniam R (2007) Indian J Hist Sci 42:493
7. Balasbramaniam R (2007) Indian J Hist Sci 42:523
8. Zhang SL, Suna XJ, Donga H (2006) Mater Sci Eng A 432:324. doi:10.1016/j.msea.2006.06.057
9. Sherby OD (1999) ISIJ Int 39:637. doi:10.2355/isijinternational.39.637
10. Taleff EM, Bramfitt BL, Syn CK, Lesuer DR, Wadsworth J, Sherby OD (2001) Mater Charact 46:19. doi:10.1016/S1044-5803(00)00087-5
11. Verhoeven JD, Pendray AH (2001) Mater Charact 47:79, 423
12. Wadsworth J, Sherby OD (2001) Mater Charact 47:163. doi:10.1016/S1044-5803(01)00184-X
13. Barnett MR, Balasubramaniam R (2007) Indian J Hist Sci 42:633
14. Barnett MR, Sullivan A, Balasubramaniam R (2008) Mater Charact (accepted)
15. Bronson B (1986) Archeom 1:13
16. Heath JM (1839) J R Asiat Soc 5:390
17. Buchanan FA (1807) Journey from Madras, through the countries of Mysore, Canara and Malabar. East India Company, London
18. Jatczak JT, Girardi DJ, Rowland ES (1956) Trans ASM 49:279
19. Bastien PG (1957) J Iron Steel Inst 193:281
20. Grange RA (1971) Metall Trans 2:417. doi:10.1007/BF02663328
21. Kirkaldy JS, von Destinon-Forstmann J, Brigham RJ (1962) Can Metall Quart 1:59
22. Kumar V, Barnett MR, Balasubramaniam R, Jaikishan S (2007) Indian J Hist Sci 42:609
23. Jaikishan S, Balasbramaniam R (2007) Indian J Hist Sci 42:461
24. Voysey HW (1832) J Asiat Soc Bengal I:245; II:402
25. Verhoeven JD (1990) Mater Charact 25:221. doi:10.1016/1044-5803(90)90012-9
26. Verhoeven JD, Jones LL (1987) Metallography 20:153. doi:10.1016/0026-0800(87)90027-9
27. Vogel R (1929) Arch Eishenhüt 5:369
28. Bramley A, Haywood FW, Coopers AT, Watts JT (1935) Trans Faraday Soc 31:707. doi:10.1039/tf9353100707
29. Verhoeven JD, Gibson ED (1998) Metall Mater Trans A 29:1181. doi:10.1007/s11661-998-0245-4
30. Tsuzaki K, Tanaka K, Maki T, Tamura I (1989) ISIJ Int 75:128
31. Hyde RS, Krauss G, Matlock DK (1994) Metall Mater Trans A 25:1229. doi:10.1007/BF02652297