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The effect of austenitizing time on martensite morphologies and magnetic properties of martensite in Fe–24.5%Ni–4.5%Si alloy

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Abstract The effect of austenitizing time on the formation of martensite in Fe–24.5%Ni–4.5%Si alloy has been studied by means of transmission electronmicroscope (TEM), scanning electronmicroscope (SEM) and Mössbauer spectroscopy technique. TEM and SEM observations revealed that the martensite morphology was found to be closely dependent on the austenitizing time. The orientation relationship between austenite and thermally induced martensite was found as the Kurdjumov-Sachs type. The volume fraction changes of martensite and austenite phases, the hyperfine magnetic field of martensite phase and isomery shift values have been determined by Mössbauer spectroscopy. The Mössbauer study also revealed that the martensite volume fractions increased with increasing austenite grain size.

Introduction

In ferrous alloys at least four different morphologies of bcc (bct) martensites have been recognized with lath, butterfly, lenticular and thin plate shapes [1–5]. Among them, lath martensite has over-whelming industrial significance since it appears in most heat-treatable commercials steels [6]. The lath martensite has also advantages of strength while twin martensite displays high strength but a brittle character [7]. It is also well known that the martensite morphology of ferrous alloys depends on austenitizing temperature and time, prior deformation of the austenite matrix, chemical composition of alloys and the cooling rate [2, 4, 8]. Durlu [2] examined the effect of high austenitizing temperature on the martensite morphologies in different Fe–Ni–C alloys and found that the martensite morphology depends on the austenitizing temperatures besides the prior austenite deformation. Himuro et al. [4] investigated the effect of ausaging on the morphology of martensite in Fe–Ni–Si alloys and reported that the martensite morphology changes from lenticular to thin plate with increasing ausaging time. It is also well established that the austenite–martensite phase transformations greatly alter the magnetic properties of the austenite and martensite phases in Fe-based alloys and Mössbauer spectroscopy is known as one of the useful and most sensitive techniques to determine the volume fractions and the magnetic characters of the both phases [9–11]. The aim of the present study was to investigate the effect of austenitizing time on the formation of martensite in Fe–24.5%Ni–4.5%Si alloy by means of transmission electronmicroscope (TEM), scanning electronmicroscope (SEM) and Mössbauer spectroscopy technique.

Experimental

Fe–24.5%Ni–4.5%Si (%wt) alloy used in this study was prepared from 99.9% pure Fe, Ni and Si elements by arc melting technique under a protective argon atmosphere. Samples were austenized at 1100 °C for 24 and 45 h in

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evacuated silica capsules. Specimens were cooled in furnace to room temperature, then immersed in liquid nitrogen to induce thermally induced martensite. Bulk samples for SEM observations were polished with a 3 μm diamond paste. These samples were etched in a solution containing 10%HF + 40%HNO_3 + 50%H_2O and observations were performed in a JEOL JSM-5600 scanning electron microscope. Thin foil samples used in TEM observations were prepared from 3 mm discs electropolished by using a twin-jet polishing technique with a solution of one part perchloric acid and four parts methanol at room temperature and examined in a JEOL 3010 TEM operated at 300 kV. Foils specimens 50 μm thick for Mössbauer spectroscopy were prepared by mechanical and chemical thinning procedures. The Mössbauer spectroscopy was carried out at room temperature by using 50m Ci ^{57}Co source diffused in Rh and a Normos-90 computer programme was used to determine the parameters and relative volume fractions of the product phase.

Results and discussion

Morphological change in martensite

Figure 1 is a SEM micrograph of martensite structure formed in Fe–24.5%Ni–4.5%Si alloy sample austenized at 1100 °C for 24 h. It shows that a twinned martensite plate near a grain boundary. On the other hand same sample austenized at 1100 °C for 45 h showed a mixed morphology which consisted of lath and lenticular plates can be seen in Fig. 2.

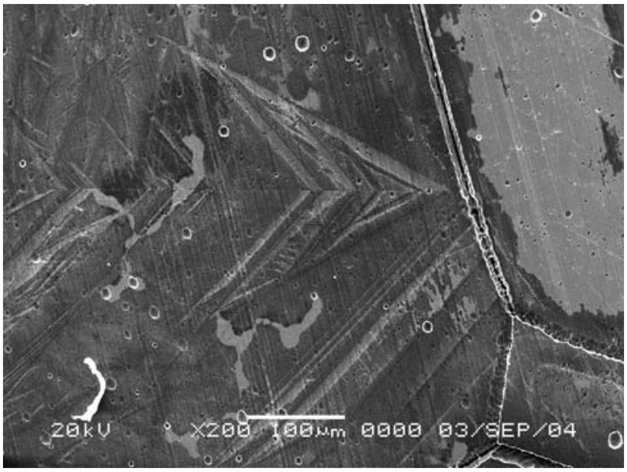

Fig. 1 SEM micrograph of martensite plate in Fe–24.5%Ni–4.5%Si alloy, austenited at 1100 °C for 24 h

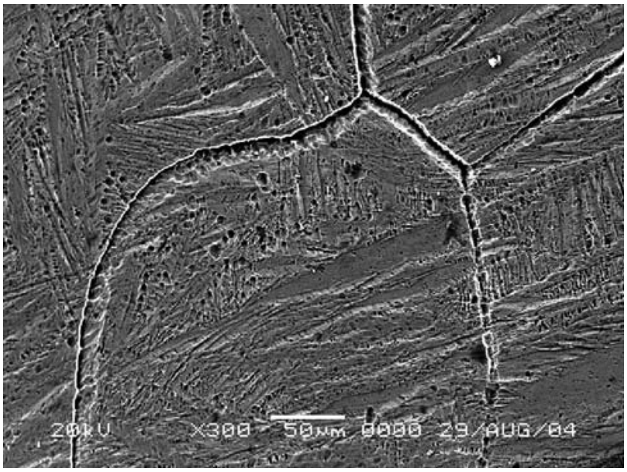

Fig. 2 SEM micrograph of martensite plate in Fe–24.5%Ni–4.5%Si alloy, austenited at 1100 °C for 45 h

Substructure of martensite

Despite the early reports on the formation of thermally induced martensite plates in ferrous alloys generally with lenticular shapes at the temperatures close to the M_s, the present observations showed the appearance of different morphologies in the examined Fe–Ni–Si alloy. Figure 3 is a TEM micrograph of martensite structures formed in Fe–24.5%Ni–4.5%Si alloy sample austenized at 1100 °C for 24 h. As shown in the figure, observed coarse martensite morphology exhibited butterfly-shaped martensite with two wings and a straight interface between them. Durlu [2] reported the formation of similar martensite wings with similar morphologies in an Fe–Ni–C alloy after the prior deformation of the austenite matrix in an early study. The present observation indicates that this typical morphology may also appear in the thermally induced martensites of an Fe–Ni–Si alloy. The selected area diffaction pattern

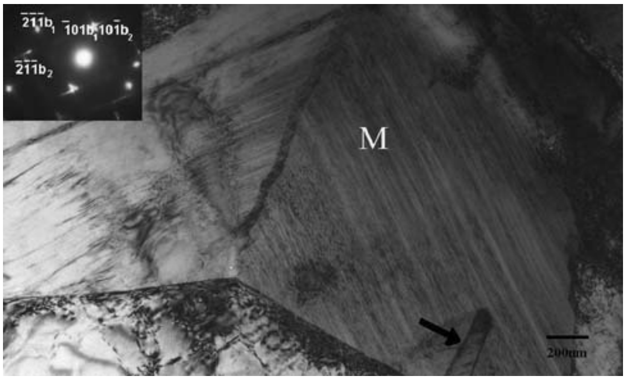

Fig. 3 TEM micrograph of the butterfly martensite formed in Fe–24.5%Ni–4.5%Si alloy with electron diffraction pattern obtained from one of the wings (marked M)

obtained from a twinned martensite plate (marked M) which consists of $[1\bar{3}1]$ martensite and $[\bar{1}3\bar{1}]$ twin zones were also given in the figure. It was revealed by the single surface analysis that the twins are formed on the {112}<111> system of the martensite crystal structure and the interface plane of the martensite wings is the {100} plane of the austenite matrix. As shown in the figure, a small martensite plate was also appeared (pointed by the arrow) in one of the large wings. Although there was no possibility of finding the twinning system of the small plate with crystallographic determinations due to its size, the direction of the observed twins in this plate was observed as parallel to the twins of the larger plate on the left as reported earlier by Durlu [2]. Figure 4 is a TEM micrograph of the plate martensite observed in Fe–24.5%Ni–4.5%Si alloy austenized at 1100 °C for 24 h. The selected area diffraction pattern of the austenite matrix and martensite (marked M) consists of [110] austenite and $[\bar{1}\bar{1}1]$ martensite zones. The orientation relationship between austenite and martensite is found as Kurdjumov-Sachs type and the habit plane was determined {252} plane of the austenite matrix. Figure 5 is another TEM micrograph of martensite plate exhibiting fine transformation twins. This sample was also austenized at 1100 °C for 24 h and the crystallographic analysis revealed that the martensite twins are formed on the {112}<111> system of the martensite crystal structure.

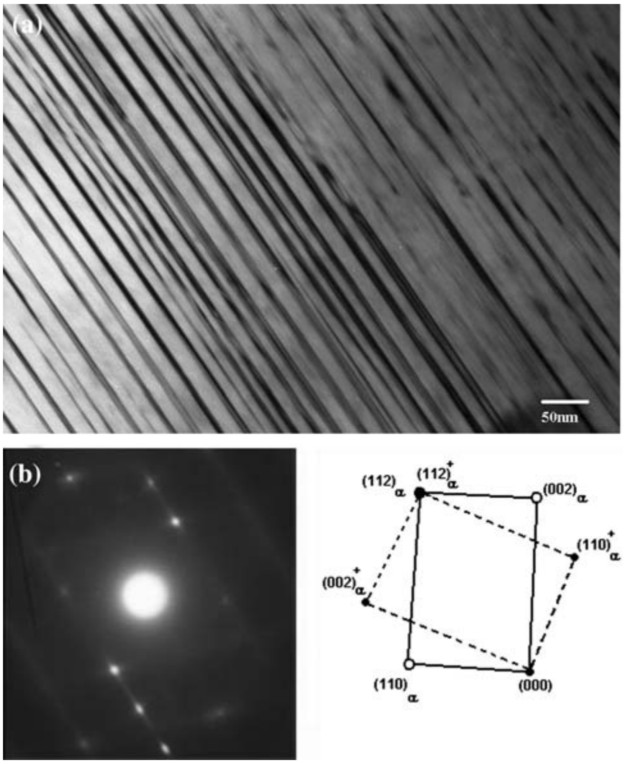

Fig. 5 (**a**) Bright field TEM micrographs of transformation twins formed in Fe–24.5%Ni–4.5%Si alloy. (**b**) Electron diffraction pattern and corresponding key diagram

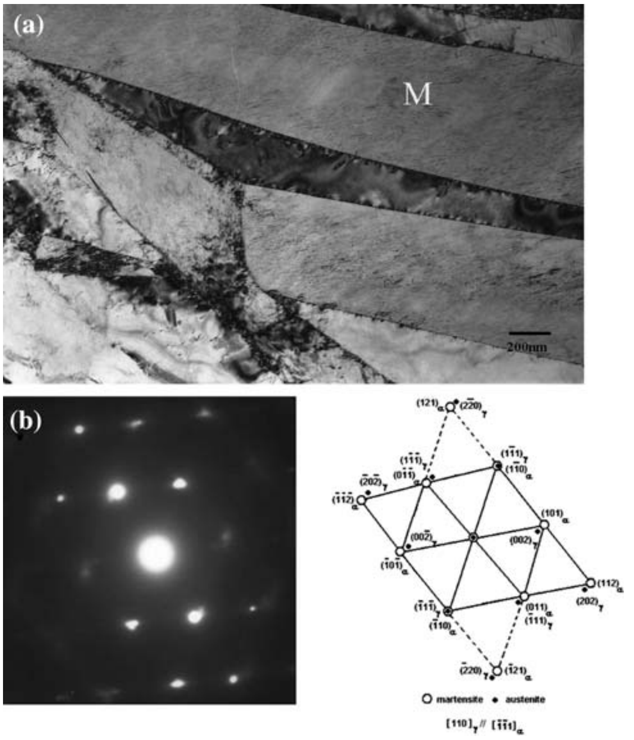

Fig. 4 (**a**) Bright field TEM micrographs of the plate martensite formed in Fe–24.5%Ni–4.5%Si alloy. (**b**) Electron diffraction pattern and corresponding key diagram

Figure 6 is a TEM micrograph of lath martensite which was observed in Fe–24.5%Ni–4.5%Si alloy, austenized at 1100 °C with a longer 45 h austenitizing time. The selected area diffraction pattern of the martensite consists of $[\bar{1}\bar{1}\bar{1}]$ martensite zones and the habit plane of the martensite was determined as the {111} plane of the matrix structure. A dense dislocation structure of the lath martensite can also be seen in the figure. As clearly shown in the micrograph the observed dislocations were appeared in a parallel configuration. Also in the same sample lenticular martensite was observed which can be seen in Fig. 7. The selected area diffraction pattern of the austenite matrix and martensite consists of [110] austenite and [111] martensite zones. The orientation relationship between austenite and martensite is found as also Kurdjumov-Sachs type and the habit plane was determined {259} plane of the austenite matrix. In addition, the thermally-induced martensite morphologies of all studied samples observed by TEM is given in Table 1.

Although the butterfly type martensites were observed after thermally and also strain-induced transformations of several Fe-based alloys [2, 12–14], they showed internal twinning only in the strain-induced case [15, 16]. The

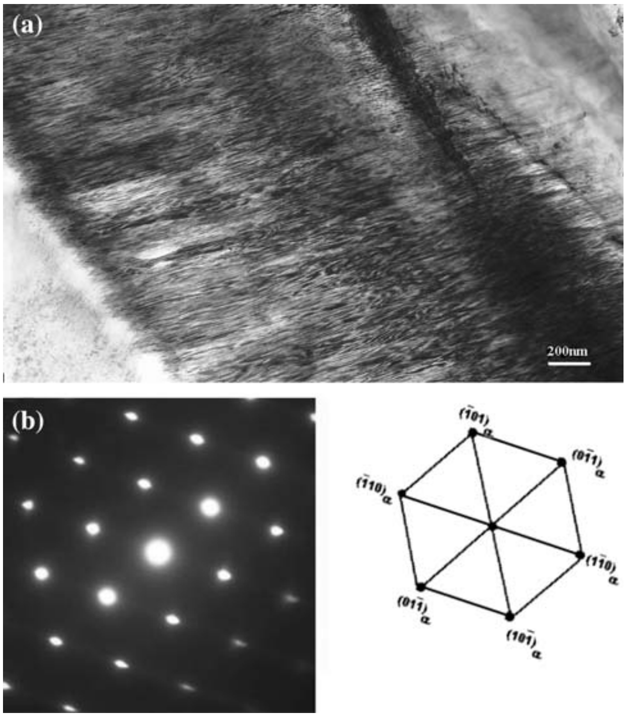

Fig. 6 (**a**) Bright field TEM micrograph of the lath martensite formed in Fe–24.5%Ni–4.5%Si alloy. (**b**) Electron diffraction pattern and corresponding key diagram

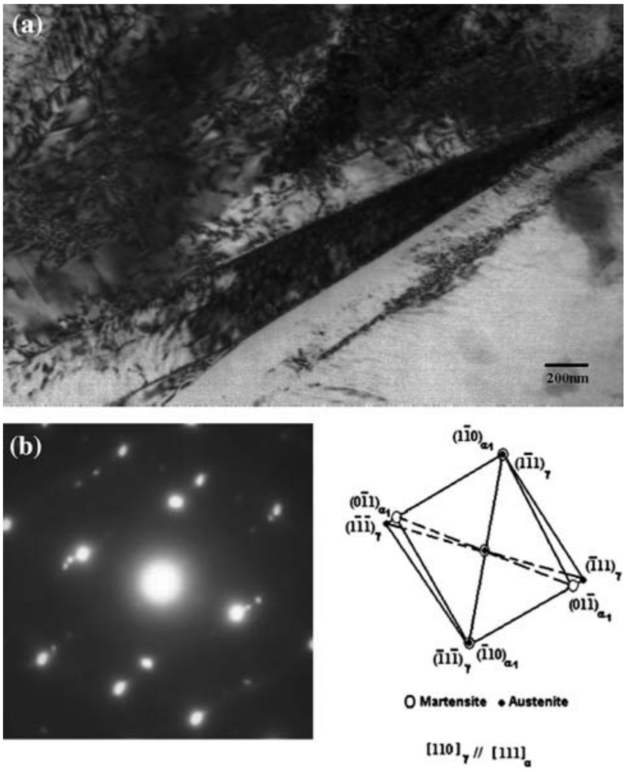

Fig. 7 (**a**) Bright field TEM micrograph of the lenticular martensite formed in Fe–24.5%Ni–4.5%Si alloy. (**b**) Electron diffraction pattern and corresponding key diagram

Table 1 Martensite morphologies for Fe–24.5%Ni–4.5%Si alloy

Temperature	Time	Observed martensite morphology
1100 °C	24 h	Butterly-transformation twinning-plate
1100 °C	45 h	Lath-lenticular

present results indicate the formation of butterfly-like plate martensites with twinned substructure under the thermally induced conditions in Fe–24.5%Ni–4.5%Si alloy. Wang et al. [17] examined the martensite formation at the temperatures lower than the usual M_s temperature of the lenticular plate martensite formation and observed some new morphologies. Present results also indicate that the plate martensites with transformation twins may be formed in Fe–24.5%Ni–4.5%Si alloy besides butterfly shaped martensite. On the other hand, Umemoto and Tamura [3] studied the interface plane in some Fe–Ni–Cr–C alloys and concluded that the butterfly wings are the kink form of the thin martensite plates which possess the two related variants of a definite habit plane and the observed interface plane is a bisecting plane for the two habit plane variants. According to their results on some Fe–Ni–C alloys the thin martensite plates were formed with {3 10 15} type habits and the interface plane was the {100} plane of austenite. The present results also revealed that the interface plane of the coupled martensite plates in the butterfly-like morphology is the {100} plane of the austenite matrix in Fe–24.5%Ni–4.5%Si alloy.

As shown in Fig. 6 the lath martensite morphologies were appeared in Fe–24.5%Ni–4.5%Si alloy with increasing austenitizing time. Jiewu et al. [7] investigated the effect of grain size in ultra-high carbon steel and found that the martensite morphology changes from twinned lath to only lath martensite without any twin formation as the austenitizing time is increased. The present observations also indicated the effect of austenite grain size on martensite morphology and showed that in Fe–24.5%Ni–4.5%Si alloy which homogenized at 1100 °C for 24 h showed the twinned martensite whereas the same alloy homogenized at 1100 °C for 45 h exhibited lath and lenticular martensite.

Magnetic properties of martensite

Mössbauer spectra obtained for the examined samples at room temperature are shown in Figs. 8 and 9. Figure 8 is the Mössbauer spectrum of Fe–24.5%Ni–4.5%Si alloys austenited at 1100 °C for 24 h and exhibits a typical six-line spectrum of the ferromagnetic or antiferromagnetic structure and also a singlet corresponding to the matrix austenite [9–11]. The Mössbauer spectrum of Fe–24.5%Ni–4.5%Si alloys was austenited at 1100 °C for 45 h

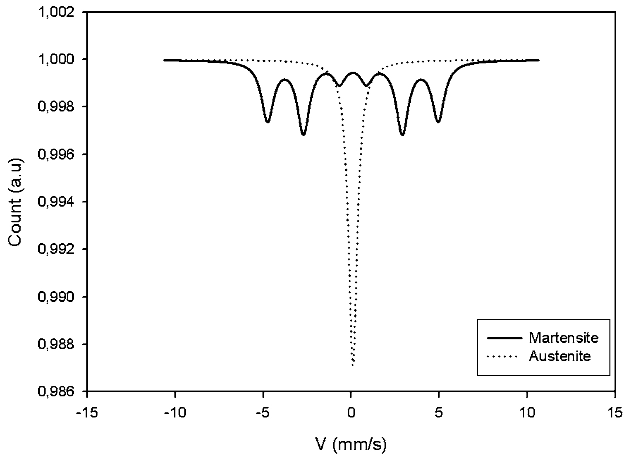

Fig. 8 Mössbauer spectrum of Fe–24.5%Ni–4.5%Si alloy, austenited at 1100 °C for 24 h

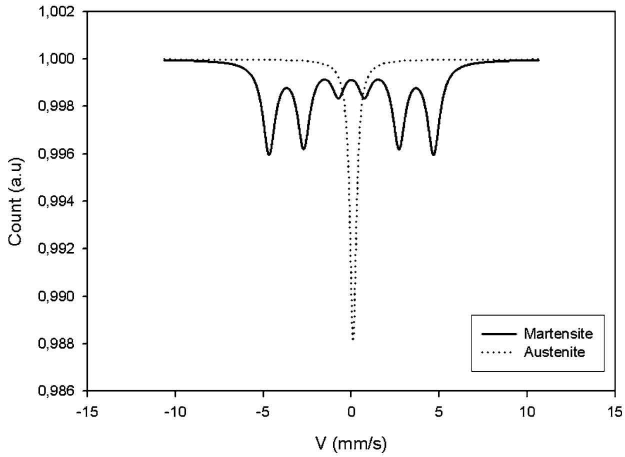

Fig. 9 Mössbauer spectrum of Fe–24.5%Ni–4.5%Si alloy, austenited at 1100 °C for 45 h

also given in Fig. 9. Martensite volume fractions were determined by using Mössbauer results and the calculated isomer shifts of the austenite and martensite phases, hyperfine magnetic field of the product martensite phase is given in Table 2. The amount of martensites in Fe–24.5%Ni–4.5%Si alloy austenited at 1100 °C for 24 h are also given in the same Table and they were found as 58.31% for 24 h and as 73.96% for 45 h austenitizing times from Mössbauer Spectroscopy measurements. It was revealed by the Mössbauer results that the amount of martensite was increased with the increasing austenitizing time while hyperfine magnetic fields of the martensitic phase was decreased. Zeng et al. [8] reported that as the alloy reaches to a more homogenized state at the higher temperatures the austenite grains are formed in relatively larger volumes and their crystal structures become more perfect. Obviously the barriers in front of the martensite growth are reduced under these circumstances and much bigger martensite crystals can be formed. However in the present study, average austenite grain size changed from 400 μm to 500 μm with increasing austenitizing time and it was found that the amount of martensite increases with an increase in the austenite grain size as expected. This result also shows the thermally stabilized character of austenite phase in relatively small grains. The decrease in the hyperfine magnetic field (H) indicates a decrease in the magnetic moment which can be attributed to an increase in the electron transfer to the unfilled 3d bands [18, 19]. The present study revealed that the amount of martensite was increased with increasing austenitizing time and the hyperfine magnetic field of the martensite was decreased in larger martensite volume fractions.

Conclusions

Results of investigations on the effect of the effect of austenitizing time on martensite morphologies and magnetic properties of martensite in Fe–24.5%Ni–4.5%Si alloy lead us to the following conclusions:

(1) Formation of butterfly-like plate martensites with twinned substructure have been observed with thermally-induced case in this study.

(2) Different martensite morphologies such as butterfly, transformation twinning and plate can be seen in the same alloy with same heat treatments. (See Table 1)

(3) Martensite morphology was changed from martensite crystal having transformation twins and plate martensite to lath and lenticular martensite with increasing austenitizing time. Due to this case it can be concluded that martensite morphology is greatly depends on austenization time at a constant austenization temperature. (See Table 1)

Table 2 Mössbauer parameters for Fe–24.5%Ni–4.5%Si alloy

Temperature	Time	δ_A (mm/s)	δ_M (mm/s)	%M	%A	H (T)
1100 °C	24 h	0.093 ± 0.018	0.09 ± 0.05	58.31	41.69	30.09 ± 0.42
1100 °C	45 h	0.1 ± 0.053	0.09 ± 0.04	73.96	26.04	29.02 ± 0.34

H (T) is the hyperfine magnetic field in Tesla, δ is the isomer shift, %M and %A are the volume fractions of martensite and austenite, relatively

(4) Increasing of austenization time increased thermally induced martensite volume fraction in related samples. (See Table 2)

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References

1. Seo SB, Jun JH, Choi CS (2000) ISIJ Int 34:91
2. Durlu TN (2001) J Mater Sci 36:5665
3. Umemoto M, Tamura I (1982) In: Delaey L, Chandrasekaran M (eds) Proceedings of the international conference on martensitic transformations, 1982 (ICOMAT 82). Belgium, p C4-523
4. Himuro Y, Kainuma R, Ishida K (2002) ISIJ Int 42:184
5. Durlu TN (1996) J Mater Sci Lett 15:1510
6. Morito S, Tanaka H, Konishi R, Furuhara T, Maki T (2003) Acta Mater 51:1789
7. Jiewu Z, Yan X, Liu Y (2004) Mater Sci Eng A385:440
8. Zeng DC, Tan YH, Qiao GW, Chuang YC (1994) Z Metallkunde 85:203
9. Zararsiz A, Gedikoglu A, Durlu TN (1981) Scripta Metall 15:595
10. Durlu TN (1992) J Mater Sci Lett 11:702
11. Aydin A, Guler E, Aktas H, Gungunes H (2002) Bull Mater Sci 25:359
12. Tamura I, Maki T, Hato H (1969) J Jpn Inst Metals 33:1376
13. Durlu TN (1996) J Mater Sci 31:2585
14. Zhang XM, Gautier E, Simon A (1989) Acta Metall 37:487
15. Gautier E, Zhang J, Zhang X, Hu TR (1994) In: Johnson WC, Howe JM, Laughin DE, Soffa WA (eds) Proceedings of the international conference on solid solid phase transformations, July 17–22, 1994, The Minerals, Metals and Materials Society, Pennsylvania, p 847
16. Durlu TN (1978) Acta Metall 26:1855
17. Wang S, Wen YH, Zhang X (1993) In: Wayman CM, Perkins J (eds) Proceedings of the international conference on martensitic transformations, 1992 (ICOMAT 92). Monterey Institute for Advanced Studies, Monterey, California, p 281
18. Panissod P, Durand J, Budnick JI (1982) Nucl Instr Methods 199:99
19. Yamauchi K, Mizoguchi T (1975) J Phys Soc Jpn 39:541