New observations on formation of thermally induced martensite in Fe–30%Ni–1%Pd alloy

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Abstract. Kinetical, morphological, crystallographical and thermal characteristics of thermally induced martensite in an Fe–30%Ni–1%Pd alloy has been studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and X-ray diffraction method. Kinetics of transformation was found to be as athermal. SEM and TEM observations and X-ray method revealed α' (*bcc*) martensite formation in the austenite phase of alloy by thermal effect. The crystallographic orientation relationship between austenite and α' (*bcc*) martensite was found to be having Kurdjumov–Sachs (K–S) type relationship. In addition, the lattice parameters of austenite and martensite phases were calculated from X-ray diffraction patterns.

Keywords. Fe–Ni–Pd alloy; martensitic transformations; electron microscopy; X-ray diffraction; athermal kinetics.

1. Introduction

Among materials scientists, there is continual interest in studying martensite and martensitic transformation. This is dictated by some beneficial properties of the martensite products (Nishiyama 1978; Krauss 1990; Bhadeshia 2004; Han and Xu 2006). Early studies on the formation of martensite in different ferrous alloys revealed that the formation mechanism and substructure of martensite are considerably altered by the transformation temperature, alloy composition, strengths of the material in the austenite and martensite phases, cooling rate of the matrix structure during the transformation and the austenite stacking fault energy in addition to the well known effects of the austenite grain size and the formation sequence of the martensitic structures (Davies and Magee 1971; Thomas 1971; Krauss and Marder 1971; Durlu 2001).

Martensitic transformation on cooling begins at the M_s temperature; the extent of transformation progressively increases with lowering of temperature and it is completed, finally attaining complete transformation at the temperature, M_f , which is known as the martensite finish temperature (Banerjee and Mukhopadhyay 2007). In many of the martensitic transformations discussed so far, the reactions start at the M_s temperature and proceed while the temperature is falling. When the cooling is stopped, the reaction stops and when the cooling is resumed, they start again. The reactions proceed only when the temperature is changing (Nishiyama 1978). Therefore, martensite produced by this type of reaction is referred to as athermal martensite. In some cases,

however, martensites form isothermally above or below the M_s temperature. This type of martensite is referred to as isothermal martensite (Nishiyama 1978).

The diffusionless *fcc* (γ) $\rightarrow$ *bcc* (α') transformation in Fe–Ni alloys has been the subject of the numerous investigations (Chilton and Kelly 1968; Maki *et al* 1984). The morphology of the resulting martensite depends on the M_s temperature, alloy chemistry, austenite yield strength and stacking fault energy (Sridharan *et al* 1991). Addition of Mn, Cr, Ti, etc as third alloying elements to binary Fe–Ni alloys alters some aspects of martensitic transformations. Especially, kinetics of transformation, morphology and crystallography of the existing martensite show a distinct variety because of the above different alloying elements (Kato and Mori 1976; Hall and Winchell 1977; Kakeshita *et al* 1993; Visvesvaran 1996).

Although many studies are present for thermally induced martensite in various Fe–Ni–X alloys, no work has been reported for the Fe–30%Ni–1%Pd alloy. Therefore, the present study was to examine morphology, crystallography and martensite kinetics of thermally induced martensite in Fe–30%Ni–1%Pd alloy by SEM, TEM, DSC and X-ray diffraction methods.

2. Experimental

The alloy employed in the present study was Fe–30%Ni–1%Pd (wt%) which was prepared by vacuum induction melting under an argon atmosphere from pure (99.9%) alloying elements. This alloy was having the shape of cylindrical bars (1 cm diameter and 10 cm long). Bulk samples were

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homogenized at 1100 °C in quartz tube for 6 h and then quenched in water at room temperature. These samples were then mechanically thinned for SEM observations. The surface of the samples was mechanically polished and used as chemical solution which contained 90 ml H_2O_2 , 15 ml H_2O and 5 ml HF for clarifying samples surfaces. Surface studies of samples were carried out using a JEOL JSM 5600 type scanning electron microscope with 20 kV operating voltage. New thin foil samples ($\sim 50 \mu\text{m}$) were prepared for transmission electron microscopy from the thermally treated samples. These TEM specimens were then electropolished at room temperature using a twin-jet polishing technique with a solution of 150 ml 2-butoxy ethanol, 50 ml of perchloric acid and 300 ml methanol. TEM observations were performed by a JEOL 3010 type TEM with 300 kV operating voltage. In order to determine M_s , A_s and A_f temperatures of transformation in Fe–30%Ni–1%Pd alloy, homogenized samples of this alloy were prepared in the shape of 1 mm diameter discs and encapsulated in aluminum pans. DSC samples of this alloy were performed by using a Perkin–Elmer Sapphire model thermal analyser and taken at a cooling rate of 5 °C/min between 20 and –150 °C.

3. Results and discussion

Figure 1(a) shows secondary electron image of SEM micrograph of the austenite phase of Fe–30%Ni–1%Pd alloy with its typical austenite grain boundaries. Figure 1(b) shows a SEM micrograph of this sample after 5 s liquid nitrogen (–196 °C) immersion. This thermal stimulation caused martensite plates formation in figure 1(b).

Martensite start temperatures (M_s) of martensite transformation ($\gamma \rightarrow \alpha'$) was determined by differential scanning calorimetry (DSC) measurements as –33 °C (figure 2a). Some evidences such as new nucleation sites or growth of existing martensite crystals achieved by further isothermal martensitic transformations are well described by Kajiwaru (1992). Although sample of the Fe–30%Ni–1%Pd alloy were kept at –196 °C for 10 min, 10 h and 10 days, these isothermal holding times did not cause the formation of martensite crystals. This application suggests that the martensite kinetics displayed athermal type. On the other hand, austenite start (A_s) and finish temperature (A_f) of transformation were also determined as 360 °C and 450 °C, respectively (figure 2b) from DSC measurements.

As a remarkable result, A_s and A_f did not show a major deviation with addition of 1% Pd to Fe–30%Ni binary alloy when compared with Kaufman's previous study (table 1) on Fe–30.7%Ni alloy (Kaufman and Cohen 1956). On the other hand, previous results have been reported that, addition of Cr, Mo and Si as a third alloying element to binary Fe–Ni alloys, the M_s temperatures of thermally induced martensites were determined as –138 °C for Fe–29.40%Ni–2%Cr alloy (Visvesvaran 1996), –180 °C for Fe–28%Ni–7.5%Si alloy (Himuro *et al* 2002) and –83 °C for Fe–30%Ni–0.8%Mo

Figure 1. SEM micrographs showing microstructure of Fe–30%Ni–1%Pd alloy: (a) austenite phase which has typical grain boundaries and (b) surface relief of martensite plates formed on immersing in liquid nitrogen.

alloy (Yasar *et al* 2006). According to the present study, compared with the other elements (Cr, Si, Mo), the element of Pd increases the temperature of M_s .

TEM observations revealed that in the examined Fe–30%Ni–1%Pd alloy the austenite matrix transforms to α' martensite. It is well known that the martensitic transformation nucleation starts at dislocations (Nishiyama 1978). Figure 3 shows TEM micrograph of a typical dislocation network in Fe–30%Ni–1%Pd alloy.

In ferrous alloys five types of *bcc* (or *bct*) martensite morphologies have been observed: lath, butterfly, plate, lenticular and thin-plate (Maki 1990). The martensite morphology depends on the alloy composition or the formation temperature. Each morphology is different in crystallography and substructure (Maki 1990; Shibata *et al* 2009). Exemplary, Fe–Ni–Ti alloys with a Ni content in the range 27 to 30 wt % form martensite i.e. tetragonal crystal structure (Whiteman and Sarma 1974). Also, addition of Mo to binary Fe–30%Ni alloys, martensite morphology was changed from

Figure 2. (a) DSC curves showing M_s temperature of thermally induced martensite in Fe–30%Ni–1%Pd alloy and (b) A_s and A_f temperatures of thermally induced martensite in Fe–30%Ni–1%Pd alloy.

Table 1. DSC results of previous and present studies.

Sample (wt%)	M_s (°C)	A_s (°C)	A_f (°C)
Fe–30%Ni–1%Pd (present study)	–33	360	450
Fe–30.7%Ni (Kaufman's study)	–42	365	435

martensite crystal having internal twins to ε -martensite with increasing Mo content (Yasar *et al* 2007). The present study shows that, addition of Pd element to binary Fe–30%Ni alloy, the austenite matrix transforms to α' -martensite. Figure 4 shows that the present observations indicate that this typical morphology may also appear in the thermally induced martensite plate of an Fe–Ni–Pd alloy. In addition, selected area electron diffraction pattern of austenite–martensite interface and matching key diagram of this pattern can be seen in figure 4(b).

It is well known that three different orientation relationships (i.e. Kurdjumov–Sachs (K–S), Nishiyama–Wassermann (N–W), and Greninger–Troiano (G–T)) between the martensite and the parent phase (austenite) have

Figure 3. TEM micrograph of a typical dislocation network in austenite phase in Fe–30%Ni–1%Pd alloy.

Figure 4. (a) Dark-field electron micrograph of athermal plate martensite and (b) selected area (indicated with a square) electron diffraction pattern and corresponding key diagram.

been reported in Fe–Ni alloys (Nishiyama 1978). It is quite obvious from figure 4(b) that the crystallographic orientation relationship between the austenite and thermally induced plate martensite crystals shows a typical $(\bar{1}\bar{1}0)_{\alpha'}/(\bar{1}11)_{\gamma}$, $[111]_{\alpha'}/[110]_{\gamma}$ Kurdjumov–Sachs (K–S) type and the habit plane is determined as very close to $[252]_{\gamma}$ plane of the austenite. These crystallographic results of study display appropriate behaviours with respect to earlier reports (Yang and Wayman 1992; Yasar *et al* 2007). Moreover, figure 5 (a–b) shows a TEM micrograph of a martensite formation

Figure 5. (a) Bright, (b) dark field electron micrographs of martensite plate with twinning and (c) electron diffraction pattern of selected area.

with twinning. In addition, figure 5(c) shows selected area electron diffraction pattern of this twinning and its corresponding indices. The electron diffraction pattern consists of two sets of reflections which correspond to the $[1\bar{1}0]$ and $[1\bar{1}0]'$ zone of the martensite crystals structure. The observed existence of the dense twinning on $\{112\}_{\alpha'}$ planes consisted of the predictions of the crystallographic theories (Wechsler *et al* 1953; Bowles and Mackenzie 1954; Mackenzie and Bowles 1954, 1957).

Crystal structures of alloy specimens were confirmed by X-ray diffraction measurement. Diffraction patterns of X-ray were also given in figure 6. As shown in figure 6, X-ray diffraction patterns exhibit the *fcc* (γ) and *bcc* (α') peaks. The mean values of the lattice parameter of the austenite and

Figure 6. X-ray diffraction patterns for each specimen of Fe–30%Ni–1%Pd alloy: (a) specimen quenched in water and at room temperature and homogenized at 1100 °C for 6 h and (b) specimen after 5 s liquid nitrogen (–196 °C) immersion.

martensite phases were calculated as 3.5712 Å and 2.8615 Å, respectively. The results of X-ray experiments agree with TEM and SEM observations.

4. Conclusions

The main findings of the present study can be summarized as:

- (I) According to DSC results, A_s , A_f and M_s temperatures do not display a major deviation with addition of 1%Pd to Fe–30%Ni binary alloy and the $\gamma \rightarrow \alpha'$ transformation kinetics found as athermal, viz. martensitic phase transformation displayed the burst phenomenon in the studied alloy.
- (II) From a morphologic viewpoint, thermally induced martensite exhibits plate morphology in the Fe–30%Ni–1%Pd alloy and the crystallographic orientation between the austenite phase and thermally induced martensite exhibited a K–S type orientation relationship.
- (III) Plate-like martensite in Fe–Ni–Pd alloys is associated with internal transformation twins.
- (IV) The observed $\{112\}_{\alpha'}$ internal twins are of the proper variant to be the transformation twins of the phenomenological theory.

(V) X-ray measurement on thermally induced martensite confirmed both SEM and TEM observations of α' (*bcc*) martensite formation.

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