JOURNAL OF MATERIALS SCIENCE **37** (2002) 1429–1435

Eutectoid decomposition in Fe_2Si_5 based alloys with a small amount of 10(Pd, Pt) and 11(Cu, Ag, Au) group elements

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The addition of a small amount of Cu is effective in accelerating the $\alpha \rightarrow \beta + \mathrm{Si}$ eutectoid decomposition. Some elements (Pd, Pt, Ag and Au) that are expected to have similar chemical properties were added to an Fe_2Si_5 based alloys up to 1.0 at.% to examine whether a similar effect could be revealed. The microstructures, X-ray diffraction and differential thermal analysis (DTA) of slowly solidified or heat treated specimens were investigated in detail. The solubility of all containing elements into the α phase was less than 0.2 at.% for the slowly solidified specimen. The excess of the additive solidified as a phase of a eutectic with the Si phase. On the other hand, the solubility of these additives in the β phase was classified into two groups. The first group had higher solubility in the β phase than that in the α phase. The solubility of the other group was as low as that in the α phase. Pd and Au belonged to the former and Pt and Ag belonged to the later. The acceleration of the eutectoid decomposition was only observed in the former group but it was negligible in the later group. The existence of the eutectic melt at the annealing temperature was effective on the coarsening of the eutectoid structure but not essential for the acceleration. The eutectoid decomposition strongly depended on the solubility of these elements into the β phase. *© 2002 Kluwer Academic Publishers*

1. Introduction

The compound β-$FeSi_2$ in the Fe-Si system [1] is known as a semi-conductive phase having high thermoelectric power [2–4]. Unfortunately the β phase is not directly formed from the melt as shown in Fig. 1. To form the β phase from the $\alpha + \varepsilon$ eutectic, annealing is required after solidification. Sometimes it takes more than 3.6×10^5 s at 1073 K for complete β formation [3]. We have reported that a small amount of Cu addition in the above alloy drastically accelerated the eutectoid decomposition as well as the peritectoid transformation [5].

Takeda *et al.* reported that a small amount of Au or Pd addition into $FeSi_2$ base alloys also accelerated the peritectoid transformation [6, 7]. They concluded that the acceleration was caused by the solubility difference of the elements between the α and the β phase [6] or the existence of a ternary liquid phase with a lower liquidus temperature [7]. They claimed that the solubility of the elements was higher for the α phase than for the β phase [7]. However, in our experiments on the Cu-containing alloys, the solubility of Cu in the β phase was higher than that in the α phase [5] and also, the acceleration was observed below the liquidus temperature of the ternary alloy [8]. From the periodic table, Cu, Ag and Au belong to 10 group and Pd and Pt belong to 11 group. The binary alloy systems of Fe-X and Si-X (X = Au, Ag, Cu, Pd, Pt) have similar equilibrium phase diagrams [1]. The element X has quite low solubility in Fe in the Fe-X system and forms a eutectic with the Si phase in the Si-X system. Therefore, we can expect a similar acceleration effect with Ag and Pt additives. However, the effect of Ag and Pt has not reported. In this study we will discuss the relation of the solubility of these elements in the α and β phases and their acceleration effect on the eutectoid decomposition.

2. Experimental procedure

Various $Fe_{29.4}Si_{70.5}X_{0.2}$ and $Fe_{28.5}Si_{70.5}X_{1.0}$ (X = Au, Ag, Cu, Pd, Pt) alloys were used. The basic binary

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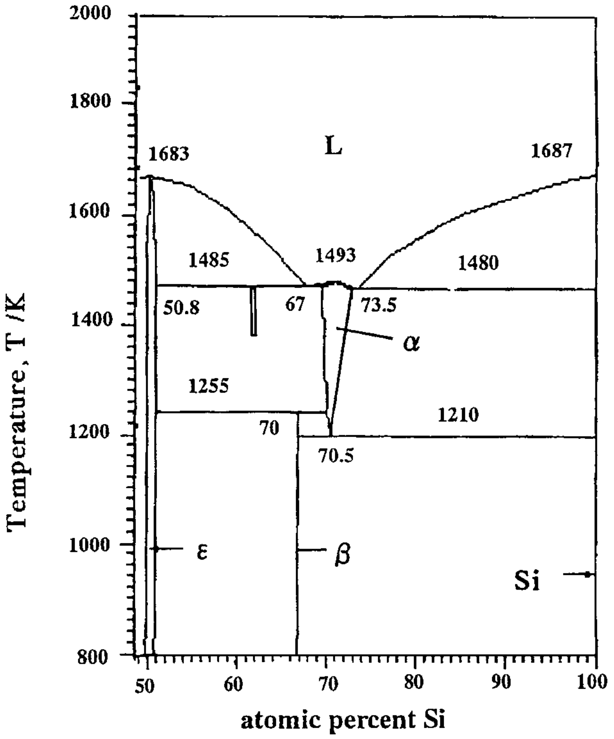

Figure 1 Equilibrium phase diagram of FeSi-Si system.

alloy composition is so close to that of the congruent of the α phase as shown in Fig. 1 [1]. The α phase can be formed as a major phase by the solidification. Therefore, the peritectic transformation ($\alpha + \varepsilon \rightarrow \beta$) will be negligible. Only a eutectoid decomposition ($\alpha \rightarrow \beta + \mathrm{Si}$) will be discussed for the β phase formation.

These alloys were prepared from 99.9 mass% electrolytic iron, high purity Si used as a semiconductor material. The purity of the additional elements was a regular grade (99.9% up). These materials were melted in an alumina crucible under Ar gas atmosphere. The molten metal was cast into a quartz tube of 3 mm in diameter by a vacuum suction method.

The microstructure was observed by BEI (back scattered electron image) of SEM without etching. The micro differential thermal analysis (DTA) was carried under Ar atmosphere to get the qualitative information for the β formation rate. In the DTA measurement, a specimen of about 25 mg was heated up to 1323 K at the rate of 0.25 K/s.

The isothermal heat treatment for the β phase was carried out at 1073 K. The fraction of the β phase was evaluated by XRD.

3. Results and discussion

3.1. Microstructure of as-solidified specimens

Fig. 2a–h shows SEM views of the as-solidified microstructures. All of the specimens showed a few secondary phase that were not observed in a binary $Fe_{29.5}Si_{70.5}$ alloy as described in a previous paper [9]. The addition of only 0.2 at.% of the third element formed the bright secondary structure. The fraction of the bright structure increased with the increase of the amount of the additives. The shape of the bright structure was usually fibrous. The granular structure was observed only in Ag containing alloys (Fig. 2c and Fig. 2g). In the alloys containing Ag or Au by 1 at.%, a dark phase was formed in the bright structure. A typical example of that structure is shown in Fig. 2h. On the other hand, there were few dark phases in the alloys containing Pd or Pt.

TABLE I Summary of EPMA for the various phases observed in slowly solidified Fe_2Si_5-1 at.%X alloys (X = Pd, Pt, Ag, Au) (at.%)

Alloy and phase	Fe	Si	X (Pd, Pt, Ag, Au)	Identified phase
1.0 at.%Pd				
Gray (matrix)	28.1	71.9	0.02	α
white	6.0	50.9	43.0	Eutectic (PdSi + Si)
1.0 at.%Pt				
Gray (matrix)	28.2	71.8	0.04	α
white	10.1	69.0	20.9	Eutectic (PtSi + Si)
1.0 at.%Ag				
Gray (matrix)	29.6	70.4	0.01	α
white	1.9	13.2	84.9	Eutectic (Ag + Si)
dark	0.3	98.8	0.9	Si
1.0 at.%Au				
Gray (matrix)	28.9	71.0	0.05	α
white	1.2	16.4	82.4	Eutectic (Au + Si)
dark	0.2	99.7	0.1	Si

X-ray diffraction patterns of these alloys are shown in Fig. 3. The pattern of a binary $Fe_{29.5}Si_{70.5}$ alloy shows that of a mono-phase for α. Some weak diffraction lines from PdSi, PtSi, Au or Ag phase can be detected in the alloys containing the additives by 1 at.%. These phases corresponded to the bright structure shown in Fig. 2. In the case of alloys containing the additives by 0.2%, the quantity of the secondary phases was too small to produce the diffraction peaks. These results shows that a new phase enriched in the third element was formed due to the low solubility of the element into the α matrix phase.

Fig. 4A and B shows the typical examples of BEI (back scattered electron image) and X-ray images by EPMA for 1.0 at.% Ag and Au containing alloys, respectively. It was clear that the bright structure observed in Fig. 2 was composed of two phases. One is the Ag or Au phase and the other is the Si phase. The iron content was negligibly small in the both phases. The quantitative results for these phases for the alloys containing the additives by 1.0 at.% are summarized in Table I. The matrix composition was close to that of the α phase and the solubility of the third elements into the matrix was very small. Most of third element was rejected from the primary α phase during the solidification and concentrated in the melt. The melt solidified as a eutectic composed of the Au or Ag enriched phase and the Si phase. Thus, a small amount of the eutectic was detected as the bright structure. In Ag or Au containing alloy, the white and dark phase corresponded to the Ag or Au phase and the Si phase, respectively, as discussed later. In the case of Pd or Pt containing alloys, the PdSi or PtSi phase was identified by XRD. A eutectic composed of the PdSi or PtSi phase and the Si phase was formed although the eutectic Si phase was difficult to observe. The average composition of the

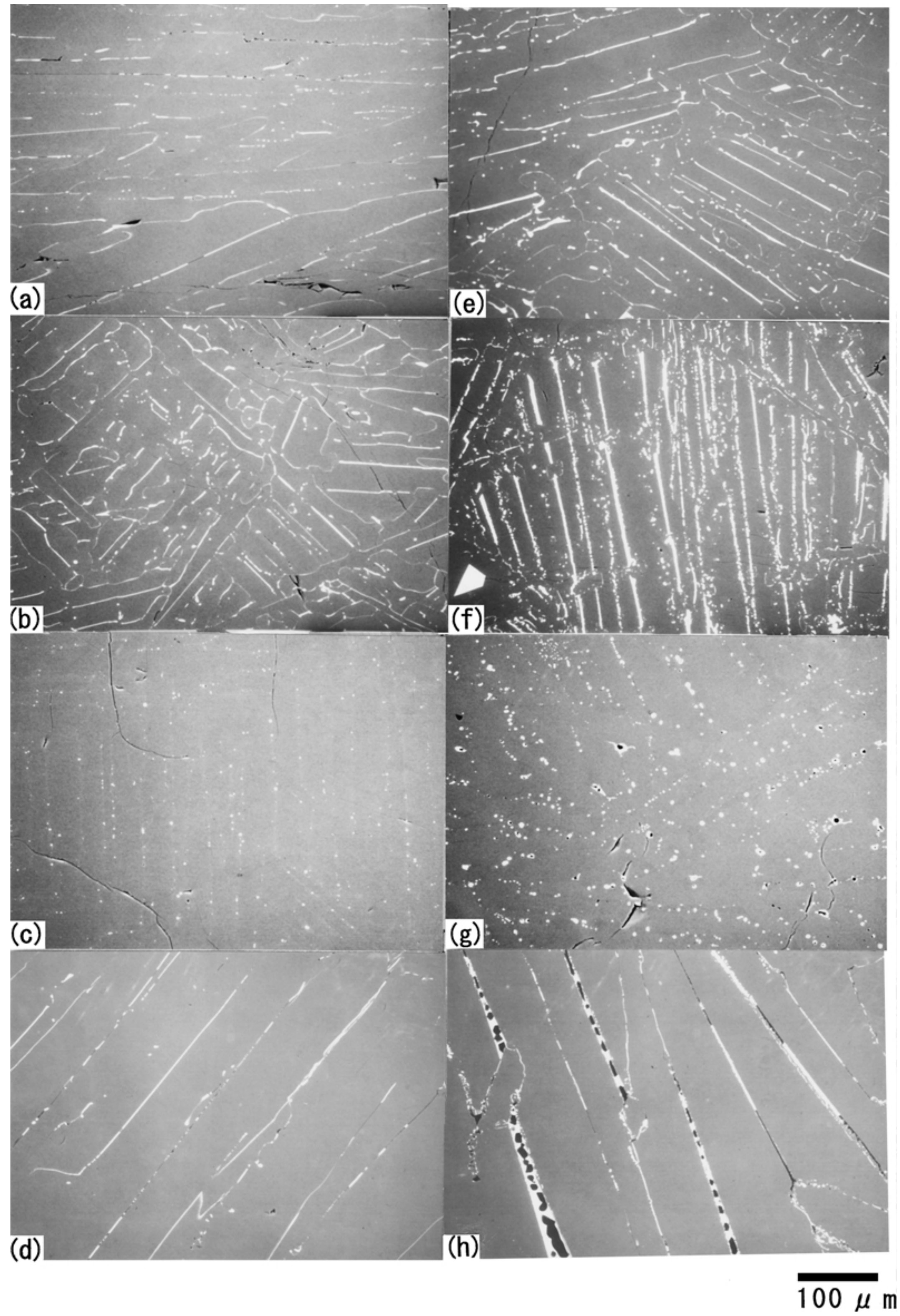

Figure 2 As-solidified microstructures of various alloys with a small amount of X element (X = Pd, Pt, Ag, Au): (a) 0.2%Pd (b) 0.2%Pt (c) 0.2%Ag (d) 0.2%Au, (e) 1.0%Pd (f) 1.0%Pt (g) 1.0%Ag and (h) 1.0%Au.

eutectic was obtained so that the analyzed Si content in the bright structure was slightly higher than that of the stoichiometric PdSi or PtSi phase.

Fig. 5 shows the DTA curves of these alloys. All alloys except the binary alloy show a small endothermic peak indicated by a small circle. These endothermic peak temperatures are shown in Table II. The temperatures were very close to the eutectic temperatures of the binary eutectic (XSi −Si or X-Si). The small difference in the temperatures may be caused by the solution of Fe in the eutectic.

As a result, all of the specimens with Pd, Pt, Ag or Au has very limited solubility of the element in the α phase. This result was similar to that found previously in the Cu containing alloy [9]. This kind of alloying addition did not cause significant difference in the solidified structures. The as-solidified structures can be qualitatively explained from the similarity of the phase diagram [1].

TABLE II Comparison of the observed endothermic temperature by DTA with the equilibrium temperature of the corresponded eutectic

Alloy	1.0 at.% Pt	1.0 at.% Pd	1.0 at.% Au	1.0 at.% Ag	1.0 at.% Cu
Observed	1280.2 K	1175 K	631.2 K	1116.3 K	1078.8 K
Binary	1252 K	1165 K	636 K	1118 K	1075 K
(eutectic)	(PtSi + Si)	(PdSi + Si)	(Au + Si)	(Ag + Si)	(η + Si)

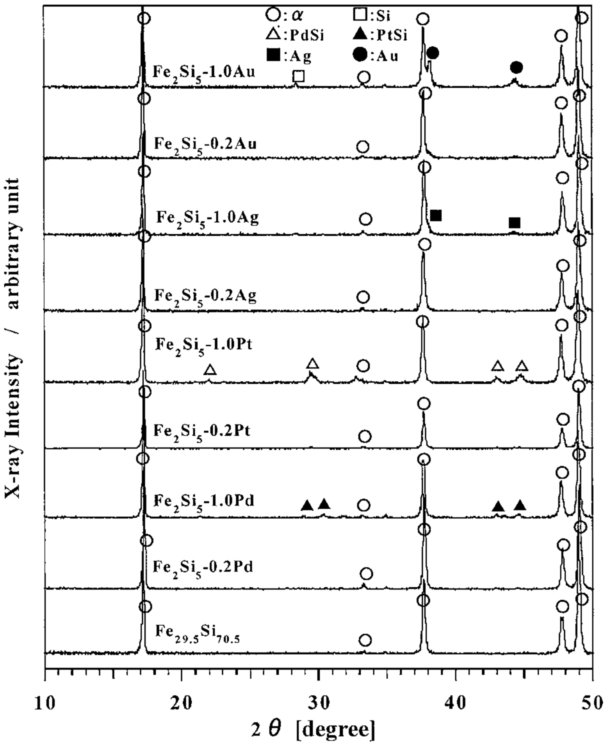

Figure 3 X-ray diffracion patterns of as-cast Fe_2Si_5 alloys with a small amount of 10 and 11 group elements.

3.2. Effect of the third elements on the eutectoid decomposition rate

The α phase is usually very stable and it was retained to room temperature during the ordinary solidification. The metastable α phase can be decomposed by heating up to the equilibrium eutectoid temperature. If the eutectoid decomposition occurs during the heating, an exothermic peak can be detected. We applied the micro differential thermal analysis (DTA) to obtain qualitative information on the stability of the α phase. The stability is inversely proportional to the decomposition rate. Fig. 6 shows the DTA curves for the various alloys. These curves can be classified into two groups. One of them shows an broad exothermic peak below the eutectoid temperature of $\alpha \rightarrow \beta + \mathrm{Si}$ and an sharp endothermic peak at the eutectoid temperature. The Cu, Au or Pd containing alloy belonged to this group. The other group shows no end/exo-thermic peaks. The Ag or Pt containing alloy belonged to this group. In the first group, the metastable α phase decomposed into the β and the Si with a broad exothermic peak and then the newly formed the β and the Si phases dissolve into the equilibrium α phase at the eutectoid temperature with a sharp endothermic peak. This sharp endothermic peak will not be present unless the eutectoid transformation occurs. No endothermic peak at the eutectoid temperature for the Ag or Pt containing alloy means that no decomposition of the α phase occurred during the heating. Therefore, the acceleration of the eutectoid decomposition was negligibly small for these alloys. Thus the kind of element may significantly affect the decomposition rate even though the as-solidified structures seemed to be similar.

The exothermic peak temperatures in the first group varied with alloys and the amount of the addition. Generally, the lower exothermic temperature under the condition of the constant heating rate, means the lower stability or higher decomposition rate. According to these criteria, the most effective element was Cu followed by Au and Pd and the effect will be accelerated by 1.0 at.% addition more than by 0.2 at.% addition.

3.3. Transformation behavior by isothermal annealing

Fig. 7 shows X-ray diffraction patterns of various alloys annealed at 1073 K for 6×10^2 s. The decomposition was completed for the 0.2 at.%Cu containing alloy but a measurable amount of the α phase remained for the 0.2 at.%Au or 0.2 at.%Pd containing alloy. The annealing temperature, 1073 K is a temperature between the eutectic temperature of the PdSi-Si eutectic (1143 K) and the Au-Si eutectic (636 K). In an Au containing alloy, the Au enriched eutectic liquid existed at the annealing temperature. On the other hand, in a Pd containing alloy, no liquid phase existed at the annealing temperature. There was no significant difference in the decomposition rate between two alloys. In the case of Cu containing alloy, the existence of a liquid phase caused the coarsening of the Si phase but no significant discontinuity in the transformation kinetics [9]. Hence the existence of the liquid phase is not essential for the acceleration of the eutectoid decomposition. This contrasts with the proposal by Kato *et al.* [6, 7]. On the other hand, no decomposition occurred for the binary, 0.2 at.%Ag or 0.2 at.%Pt containing alloy. This result was same for the 1.0 at.%Ag or 1.0 at.%Pt containing alloy. The amount of the addition of Ag or Pt was not important.

The variation of the fraction of the β phase with annealing time at 1073 K is shown in Fig. 8. A small amount of Au addition was effective in accelerating the decomposition though the effect is slightly lower than that of Cu addition. The addition of Ag did not accelerate nor delay the decomposition. The same result was obtained for the Pt containing alloy. The shape of curves in Fig. 8 was similar among various alloys. A Johnson-Mehl-Avrami equation was fitted to the data for the 0.2 at.%Au containing alloy annealed at 1073 K as shown by the curve in Fig. 8. The time exponent related to the nucleation and/or growth mechanism was 2.28 and close to that for the Cu containing alloy [9]. The kinetic coefficient related to the growth rate was varied with the additives.

3.4. Structure change by isothermal annealing

Fig. 9a–f shows the microstructures of the specimens annealed at 1073 K In a 0.2 at.%Pd (Fig. 9a)

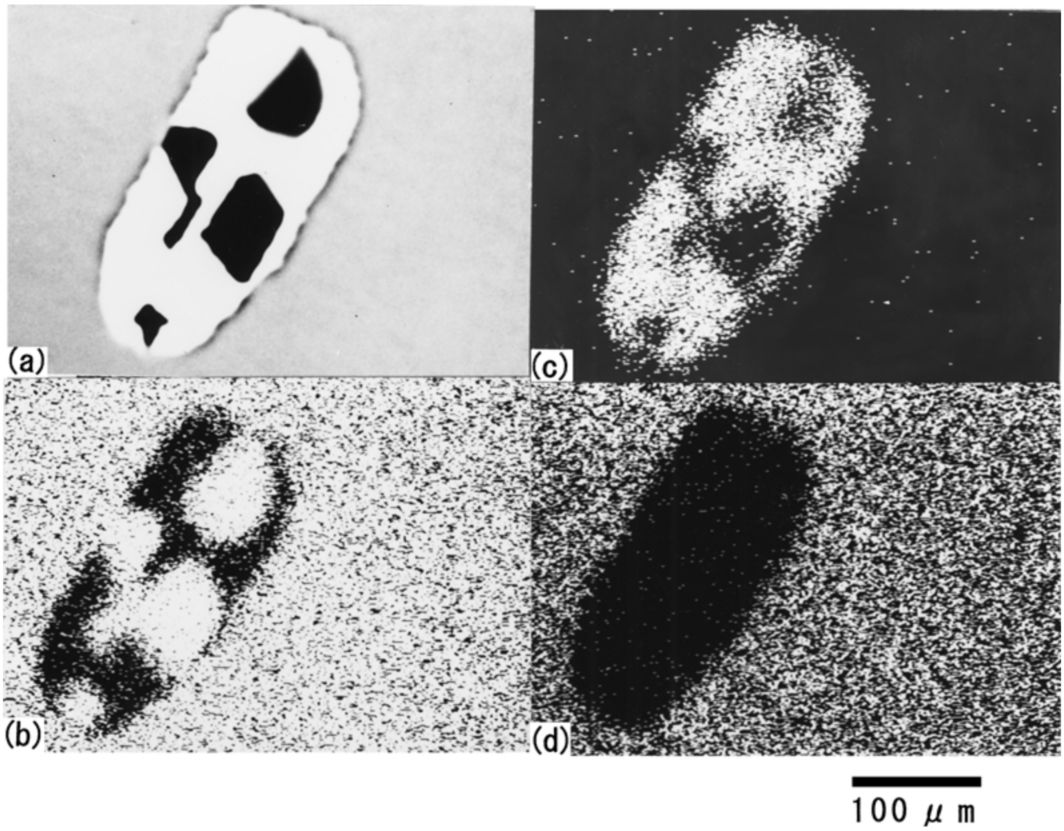

Figure 4A X-ray images of 1.0%Ag added Fe_2Si_5 alloy: (a) Composition image, (b) Si X α image, (c) Ag X α image and (d) Fe X α image.

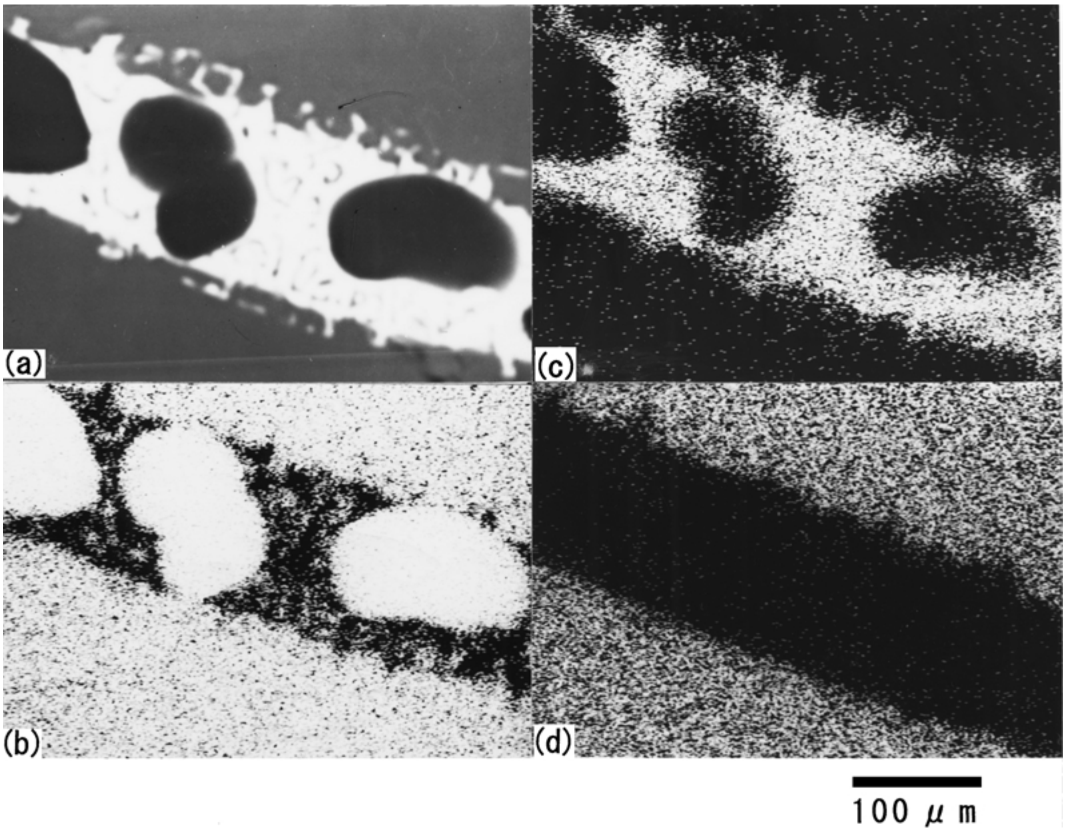

Figure 4B X-ray images of 1.0%Au added Fe_2Si_5 alloy: (a) Composition image, (b) Si X α image, (c) Au X α image and (d) Fe X α image.

containing alloy annealed for 6×10^2 s, finely lamellar and homogeneous eutectoid structure were observed and the bright structure, as shown in Fig. 2a, still remained. The bright structure was a eutectic of $PdSi + Si$. The annealing temperature (1073 K) was lower than 1175 K of the eutectic temperature of $PdSi + Si$ so the bright structure was solid at the annealing temperature. In a 0.2 at.%Au containing alloy annealed for 6×10^2 s, the structure was quite inhomogeneous. Some areas contained coarse $\beta + Si$ eutectoid.

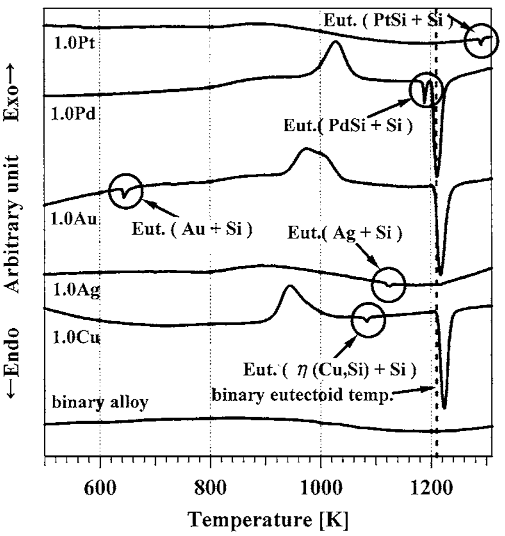

Figure 5 DTA curve of alloys including the third element by 1 at.% show a small endothermic peak marked by a circle. The peak was close to the temeperature of the eutectic composed of the X or XSi and the Si phase.

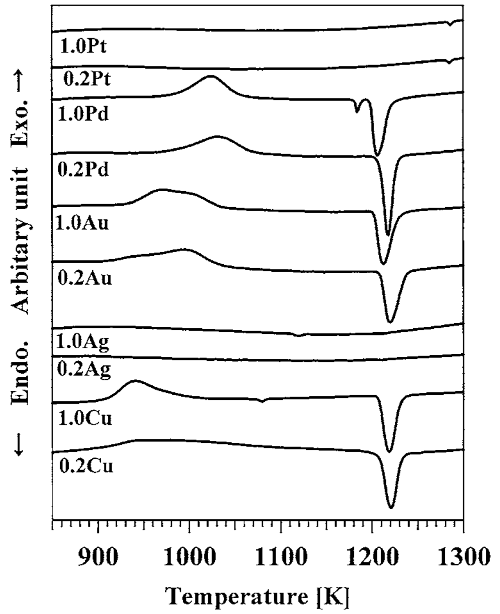

Figure 6 DTA curve of various alloys shows the effect of third element on the eutectoid decomposition rate.

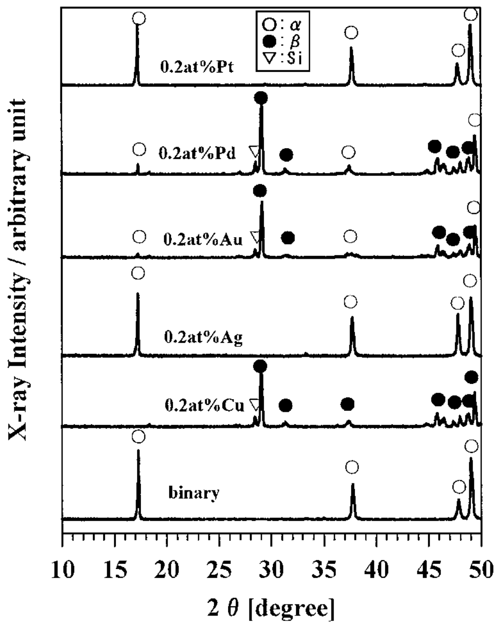

Figure 7 XRD patterns of various alloys anealed at 1073 K for 600 s.

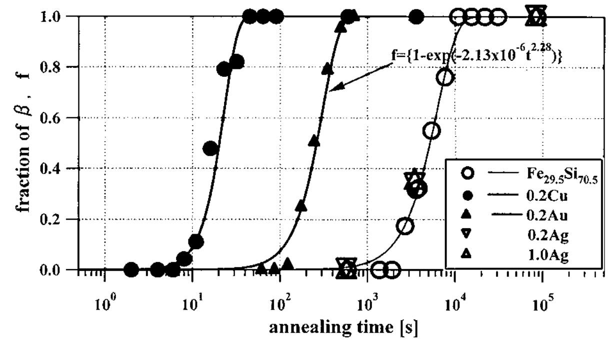

Figure 8 Variation of β fraction with annealing time annealed at 1073 K.

The fine structure of the $\beta + \text{Si}$ eutectoid started from the coarse region and stopped at un-decomposed α phase. The bright and fibrous structure degenerated by the formation of $\beta + \text{Si}$ eutectoid. Very thin and white contrast indicated by an arrow in Fig. 9b was observed at the interface between the α and the fine eutectoid. In this case, a small amount of eutectic liquid existed at the annealing temperature.

The diffusivity of Au, Si and Fe atoms in liquid state was so high that it lead to the acceleration of the dissolution of the Au + Si eutectic into the β phase and the eutectoid coarsening was enhanced. A similar result was obtained in the Cu containing alloy [9]. The eutectoid decomposition started at the location close to the Au enriched eutectic liquid region and propagated to the peripheral region. The Au enriched liquid was pushed by the growing eutectoid solid interface and some parts were engulfed into the eutectoid. The amount of the bright structure was obviously decreased in this alloy. This means that the solubility of Au in the β phase was higher than that of the α phase, essentially the quantity of the bright structure decreased with increase of the β phase.

In 0.2 at.%Pt (Fig. 9c) or 0.2 at.%Ag (Fig. 9d) containing alloy annealed for 8.64×10^4 s, where the decomposition was completed, and the decomposed structure seems to be homogeneous and finely lamellar eutectoid. The bright structure shown in Fig. 2c and Fig. 2d still remained. The solubility of Pt or Ag in the β phase was probably insignificant.

The bright structure in the Fig. 9b for the shortly annealed specimen was disappeared for the longer annealing as shown in Fig. 9e. It is concluded that the solubility of Pd in the β was high and the time to the complete dissolution of PtSi + Si eutectic took a long time because the eutectic was not liquid but solid at the annealing temperature. Similar result was shown for Au containing alloy in Fig. 9f. The dissolution rate of the eutectic into the β depended on the eutectoid melt. The solubility was too small to be analyzed quantitatively by EPMA or X-ray diffraction. The PdSi or Au phase was formed again by heating the specimen dissolved Au or Pd in the β phase above the α stable temperature. The solubility of the these additives was higher in the β phase than that in the α phase.

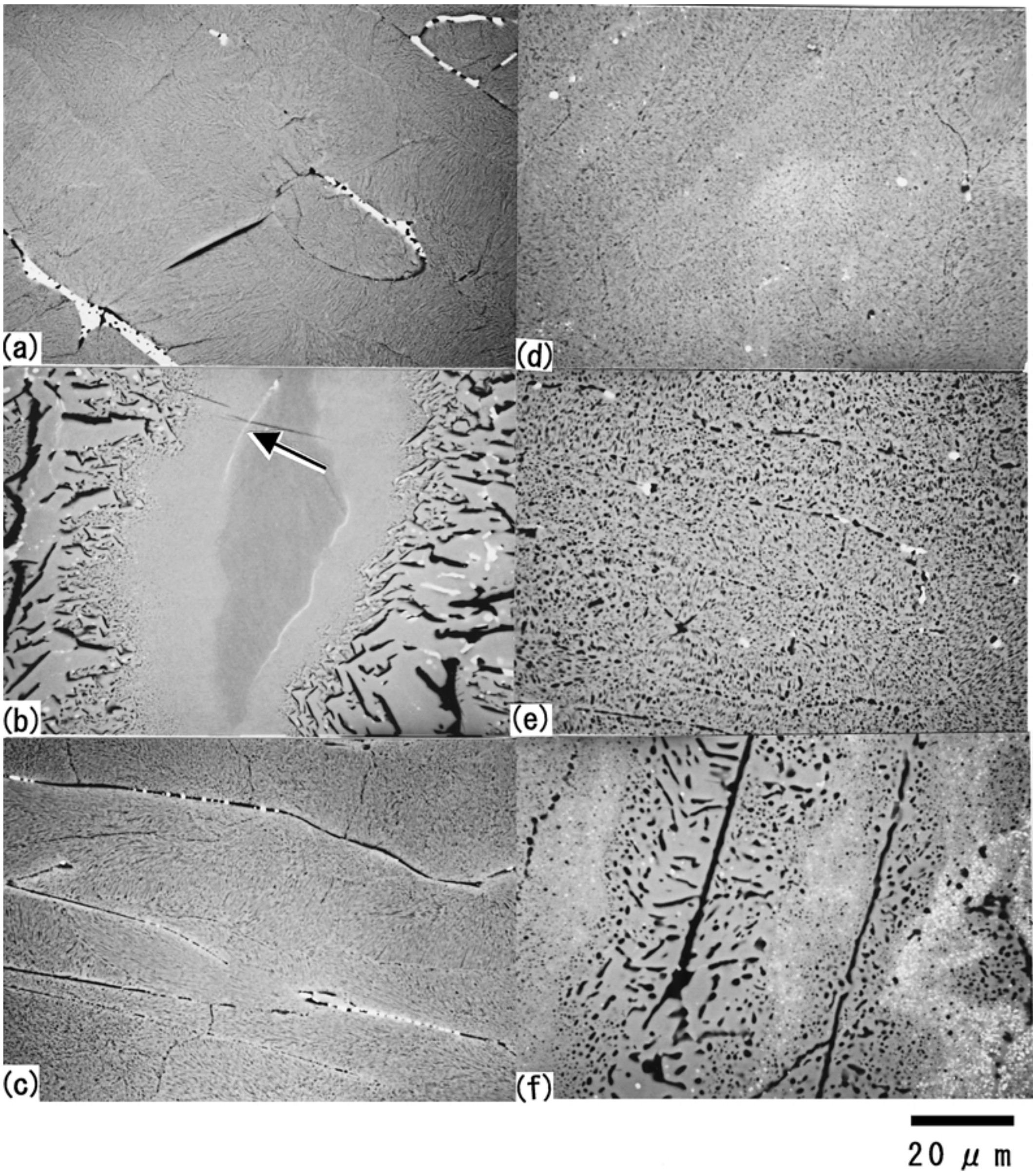

Figure 9 Micro-structures of annealed specimens at 1073 K for various time: (a) 0.2%Pd for 6×10^2 s (b) 0.2%Au for 6×10^2 s (c) 0.2%Pt for 8.64×10^4 s, (d) 0.2%Ag for 8.64×10^4 s (e) 0.2%Pd for 8.64×10^4 s and (f) 0.2%Au for 8.64×10^4 s.

The additives (Pd, Cu and Au) contributed to the acceleration of the eutectoid decomposition and they had only limited solubility in the β phase. On the other hand, the additives (Pt and Ag) did not cause the acceleration and their solubility in the β was negligibly small.

4. Conclusions

1. The solubility of the elements belong to 10(Pd, Pt) and 11(Cu, Ag, Au) group in the α phase was less than 0.2 at.% after ordinary solidification. Excess additives beyond the solubility solidified as one phase that formed a eutectoid with the Si phase.

2. A small amount of Cu, Au and Pd was effective in accelerating the eutectoid decomposition ($\alpha \rightarrow \beta + \mathrm{Si}$). In contrast Ag or Pt addition did not effect the rate of composition.

3. The existence of the eutectic or ternary liquid was not related to the acceleration.

4. The solubility of Cu, Au and Pd in the β phase was beyond 0.2 at.% and higher than that in the α phase. On the other hand, in the case of Ag and Pt, the solubility of them in the β phase was negligibly small.

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Received 15 August 2000
and accepted 21 November 2001