bcc metastable phase coexisting with the icosahedral phase in rapidly quenched $Fe_{28}Ti_{68}Si_4$ alloys

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The FeTi-Si quasicrystalline system has been investigated by systematically varying the alloy composition. A metastable bcc phase with the lattice parameter close to 1.31 nm is reported for the $Fe_{28}Ti_{68}Si_4$ alloy. Its orientational relationship with the icosahedral phase has been established based on x-ray-diffraction and electron-microscopy experiments. Electron-microscopy studies have revealed the interrelationship between the icosahedral and the cubic variants; the twofold, threefold, and fivefold icosahedral (*i*) phase axes are parallel to ⟨001⟩, ⟨111⟩, and nearly ⟨530⟩ directions of the cubic phase. A possible growth mechanism for the formation of both the icosahedral and the metastable bcc phase has been suggested. Structural transformations originating because of annealing (at 700 and 900 °C) in an argon atmosphere have been investigated. The transformation sequence has been found to correspond to $(FeTi_2)(i) \xrightarrow{700\,^\circ C} (FeTi_2)(\text{bcc, metastable}) \xrightarrow{900\,^\circ C} (FeTi_2)(\text{fcc, equilibrium}) + \beta\text{-Ti}$.

I. INTRODUCTION

Immediately after the discovery of the quasicrystalline phase in certain alloys, it was realized that these phases bear a strong structural relation with the corresponding crystalline phases.[1,2] In fact, this consideration was employed to predict the formation of the icosahedral phase in various alloys.[3–5] More direct evidence of the interrelation between crystalline and quasicrystalline phases was obtained by bringing out the orientational relationship between these phases in several alloy systems.[6–12] Recently, metastable crystalline phases have been discovered in Al-Cr-Ni and Al-Mn-Ni alloys which show an orientational relationship with the corresponding quasicrystalline phases.[10] The results of these investigations are illustrative of the fact that the local atomic configurations of quasicrystalline and crystalline phases are closely related. In the present work, a bcc metastable phase in the Fe-Ti-Si system ($Fe_{28}Ti_{68}Si_4$) has been found. Based on electron-microscopic and x-ray-diffraction explorations, its orientational relation with the icosahedral phase in the $Fe_{28}Ti_{68}Si_4$ alloy has been established. These results shed light on the growth process and atomic positions of the icosahedral phase in relation to the metastable bcc phase in rapidly quenched Fe-Ti-Si systems.

II. EXPERIMENTAL

High-purity iron, titanium, and silicon (all 99.99% purity) were taken in the correct proportions to form an alloy of the stoichiometry $Fe_{28}Ti_{68}Si_4$ and were melted and homogenized, employing rf induction furnace, in an argon atomosphere in a previously outgassed graphite crucible. Thin ribbons of the Fe-Ti-Si homogenized alloy ($\sim$2 mm in width and 40 μm in thickness) were prepared by the melt-spinning technique using a 14-cm-diam copper wheel rotating at a speed of about 4000 rpm. The melting and solidification processes were carried out in an enclosure filled with argon. The rapidly quenched alloy was characterized by the x-ray powder-diffraction method employing a Philips PW-1710 diffractometer. The ribbons were electrolytically thinned using an electrolyte of 5% $HClO_4$ in ethanol at -30° C and investigated in a Philips CM-12 electron microscope embodying a PV-9900 EDAX analyzer.

III. RESULTS

In our earlier work[15] it was found that a partial substitution of Fe by Si (6 at. %) in $FeTi_2$ suppresses the formation of the equilibrium crystalline version and stabilizes the icosahedral phase. The as-quenched $Fe_{28}Ti_{68}Si_4$ alloy exhibits a mostly icosahedral phase with a trace of the crystalline metastable phase. Figure 1 shows the XRD pattern of the as-synthesized alloy. The observed XRD peaks could be successfully analyzed in terms of the system to correspond to bcc with $a = 13.15$ Å. The intensity of the icosahedral peaks is higher than the crystalline ones (Fig. 1) indicating that the volume fraction of the crystalline phase is rather small.

A representative transmission electron micrograph of the as-spun alloy is shown in Fig. 2(a). It shows a large, roundish icosahedral grain surrounded by a narrow rim of the crystalline phase. In some other regions one side of the icosahedral grain is found embracing the crystalline grains [Fig. 3(a)]. However, in all the cases it has been noticed that the surrounding crystalline phase has a definite orientational relationship with the icosahedral phase. Figures 2(b) and 2(c) exhibit the selected-area electron-diffraction (SAD) patterns showing the twofold symmetry characteristic of the icosahedral phase and a [001] bcc pattern, respectively. Arcs of diffuse scattering can easily be noticed in Figs. 2(b) and 2(d). The latter SAD pattern corresponds to the overlapping pattern of these two phases. The ⟨001⟩ cubic directions and the twofold icosahedral axes of the patterns are exactly parallel. More specifically, it may be said that the (600)-type cubic spots coincide perfectly with the (221001)- type

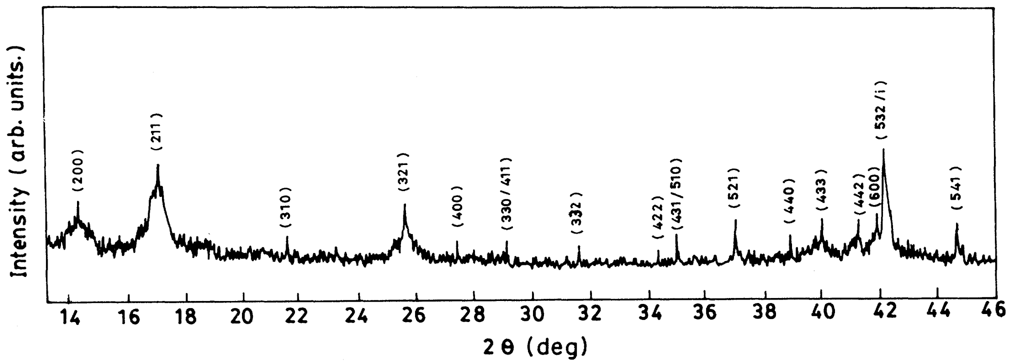

FIG. 1. X-ray powder diffraction pattern of the rapidly solidified $Fe_{28}Ti_{68}Si_4$ alloy. The analysis of the XRD peaks reveals a bcc structure with $a = 1.31$ nm for the metastable phase. One of the icosahedral peaks is exactly coincident with the (532)-type reflections of the metastable bcc phase.

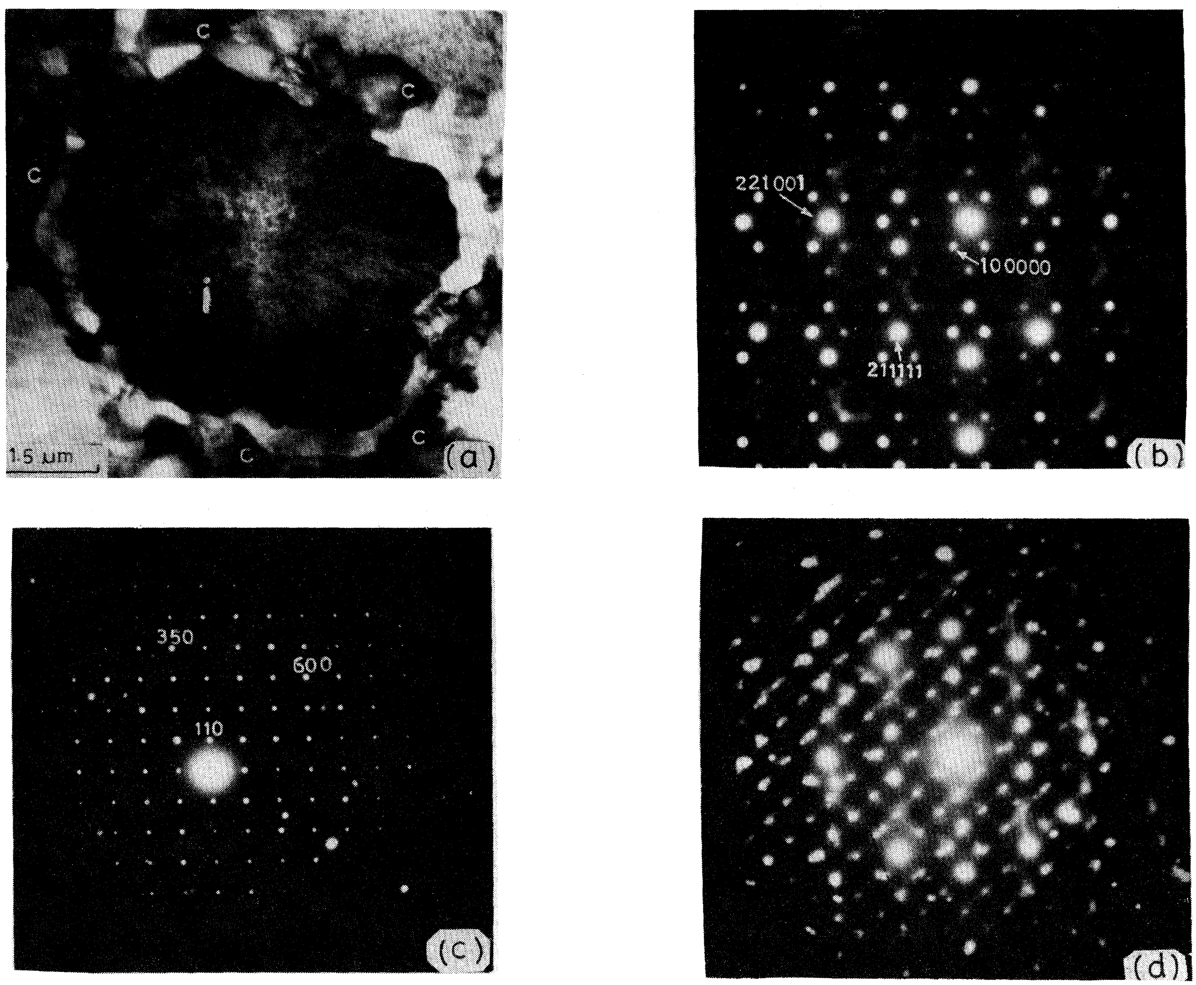

FIG. 2. (a) A representative electron micrograph of as-spun Fe-Ti-Si alloy showing a large roundish icosahedral grain surrounded by a rim of bcc crystalline grains. (b) Selected-area electron diffraction pattern showing twofold symmetry characteristics of the as-quenched *i* phase. Arcs of diffuse scattering can easily be noticed. (c) SAD pattern from ⟨001⟩ zone axis of the metastable bcc phase and (d) SAD pattern showing overlapping of reflections from the icosahedral quasicrystal and the cubic (bcc) crystal.

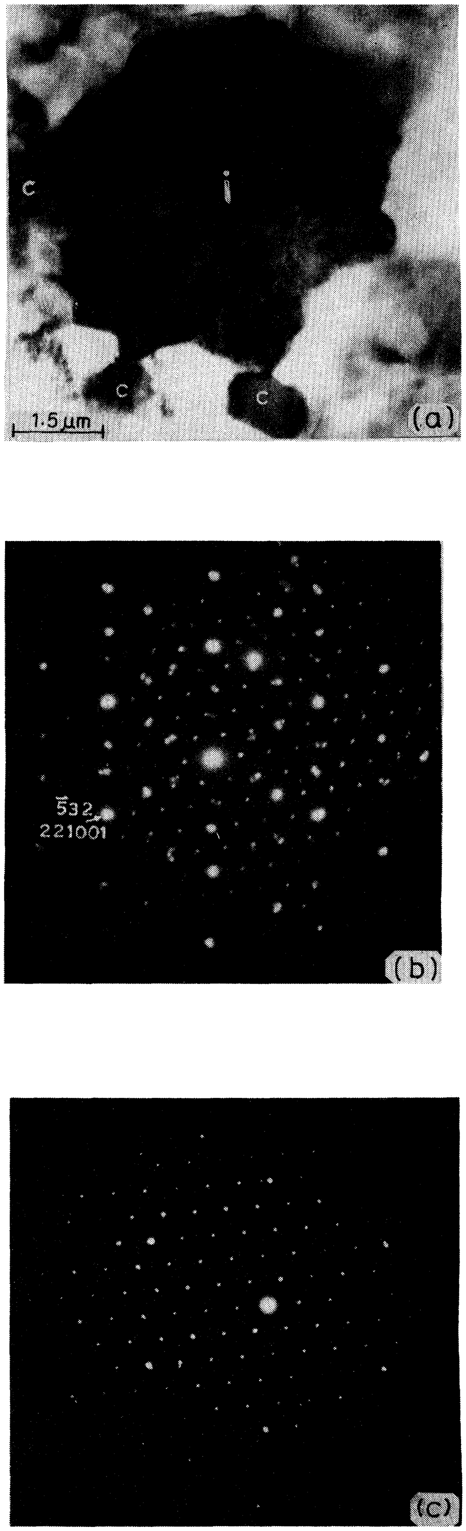

FIG. 3. (a) A representative electron micrograph of a rapidly solidified alloy showing an icosahedral grain in contact with the crystalline grains, (b) SAD pattern showing a superimposition of reflections from the *i* phase with threefold zone axis and ⟨111⟩ bcc metastable phase, and (c) SAD pattern corresponding to ⟨111⟩ zone axis of the bcc phase.

icosahedral spots. Figure 3(a) depicts the micrograph of the icosahedral and the embracing crystalline grains; Fig. 3(b) shows the overlapping diffraction pattern corresponding to the threefold zone axis. Figure 3(c) shows the ⟨111⟩ diffraction pattern from the bcc metastable phase. The threefold icosahedral direction coincides with ⟨111⟩ cubic directions [Fig. 3(b)]. In particular, the (532)-type spots of the ⟨111⟩ cubic pattern coincide closely with (221001)-type spots in the threefold icosahedral pattern. One of these coincidences of spots is marked by the arrow in Fig. 3(b).

Figure 4 shows a fivefold icosahedral pattern with an overlapping ⟨035⟩ cubic pattern. Out of the possible five cubic variants only one variant is present in this case. The fivefold icosahedral direction is nearly parallel to ⟨035⟩ directions of the cubic phase. More specifically, (532)-type spots were found to be nearly coincident with (221001)-type spots in the fivefold electron diffraction pattern. The fivefold symmetry appears broken. Instead, two mirrors can be observed in this composite pattern. Similar observations have already been reported in other alloy systems.[8,20]

The compositions of the icosahedral and crystalline grains have been determined by energy dispersive analysis of x rays (EDAX) in conjunction with STEM using a 20-nm probe of electron beam. Figs. 5(a) and 5(b) show representative energy dispersive spectra of the icosahedral and crystalline grains, respectively. The compositions of the icosahedral and crystalline phases obtained from the EDX analysis can be given as $Fe_{24}Ti_{72}Si_4$ and $Fe_{26}Ti_{70}Si_4$, respectively. In passing, it may be mentioned here that slight variations in composition [viz., (24±2) Fe (70±2.5)Ti(4±0.5)Si] have been noticed during point-to-point analysis within the grain. Similar observations have also been reported by Kim *et al.*[21] in the $Al_6Cu(Li,Mg)_3$ icosahedral phase. The above-mentioned compositions are average compositions. It has also been noticed that the icosahedral phase has always somewhat a higher titanium to iron ratio ([Ti]/[Fe]).

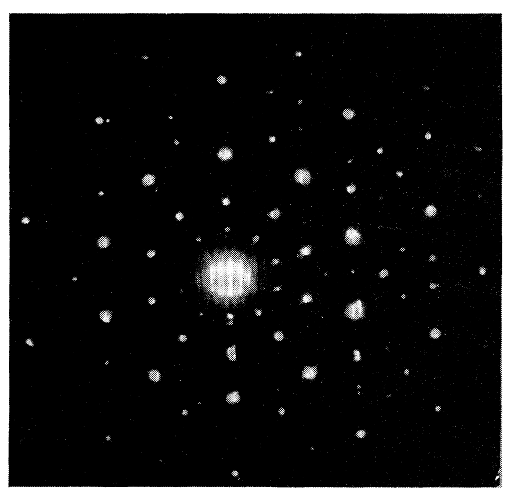

FIG. 4. Fivefold icosahedral pattern with an overlapping ⟨530⟩ cubic pattern.

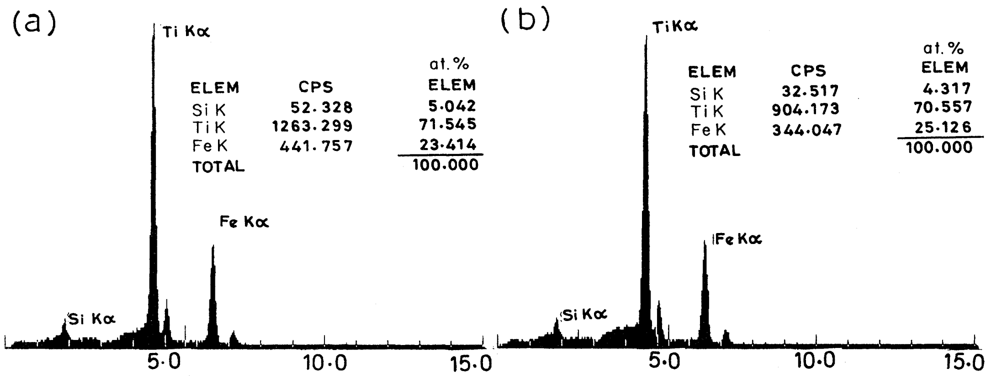

FIG. 5. Representative EDX spectra of the (a) icosahedral and (b) crystalline grains.

In order to check the thermal stability and the structural inter-relationship of the phases, the as-quenched Fe-Ti-Si alloy was annealed isothermally at 700 ($\pm$10) °C for 30 min in argon atmosphere. The XRD characterization of the annealed alloy revealed that reflections due to the metastable phase (bcc) are more pronounced. This suggests that in the annealed version the volume fraction of the metastable phase has increased in comparison to the volume fraction of the icosahedral phase. The microstructure of the annealed alloy also shows the increased volume fraction and larger grain size of the metastable phase (see Fig. 6). The composition of icosahedral and crystalline grains in annealed samples has been checked by EDAX and has been found to be the same (within experimental error) as that of the as-quenched alloy. The observed arcs representing the diffuse intensity have the same appearance after annealing at 700°C as at room temperature. After further annealing at 900°C for 30 min, the Fe-Ti-Si alloy transforms to a mixture of the known stable crystalline fcc phase and

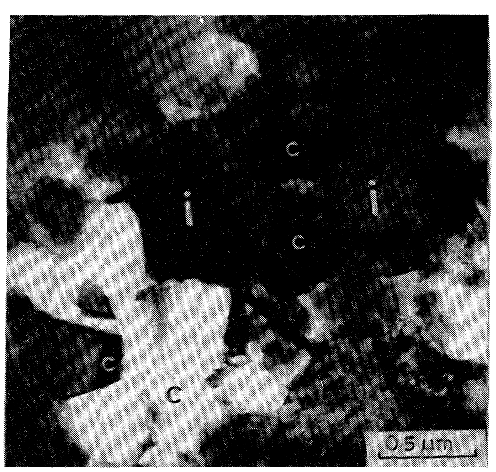

FIG. 6. A representative electron micrograph of the annealed (700°C for 30 min) Fe-Ti-Si alloy showing the larger grain size and increased volume fraction of the metastable bcc phase.

a trace of the β-Ti phase (see Fig. 7). This transformation study confirms that the bcc phase observed in the present investigation is a metastable one.

IV. DISCUSSION

It has been shown by us as well as other workers[6,13] that a rapidly solidified $FeTi_2$ alloy exhibits icosahedral phase and an equilibrium fcc crystalline phase. When Fe is substituted by 6 at. % of Si in $FeTi_2$, it results in the formation of only the icosahedral phase having a large amount of structural disorder.[15] In general, Si-substituted versions of $FeTi_2$ appear to be a highly disordered quasicrystalline material. The disorder is manifested by the occurrence of diffuse scattering in the x-ray and electron diffraction patterns[14–16] The monitoring of disorder, viz., the shape, location, intensity distribution in the arcs and details in regard to the diffuse scattering in Fe-Ti-Si system shows features which are quite similar to Ti-Mn icosahedral quasicrystals.[14]

XRD and electron-diffraction results obtained in the present investigation suggest that 4 at. % substitution of Si in a $FeTi_2$ rapidly solidified alloy results in the formation of the icosahedral phase and a bcc metastable phase with a lattice parameter close to 1.31 nm. It may be mentioned here that Dong *et al.*[22] have shown the existence of a bcc phase in the $FeTi_2$ system with the same lattice parameter. It may be possible that the sample prepared by them incorporates some Si which could have come from the silica vessel during the process of sample preparation. However, the EDX spectra of the $FeTi_2$ alloy investigated by Dong *et al.*[22] indicate the absence of Si. Instead, they found the incorporation of some Al in icosahedral as well as crystalline grains. In light of the above-mentioned observations, it may be said that we have observed the bcc metastable phase in a Fe-Ti-Si system.

The remarkable feature of this metastable phase is that it coexists with icosahedral phase having a definite coherent orientational relationship. It will be opportune to mention that a similar orientational relationship between crystalline and icosahedral phases has also been observed in Al-Mn-Si, Al-Mn-Fe-Si, and Al-Mn-Ge alloy

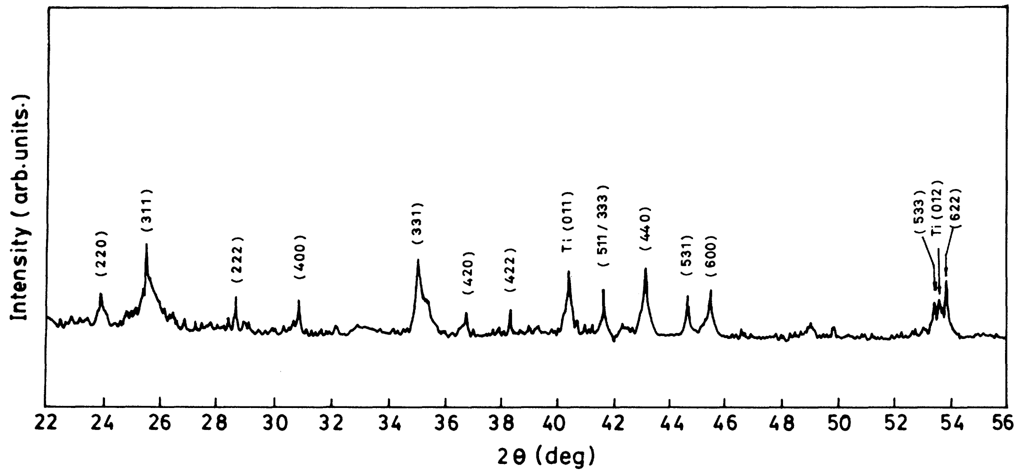

FIG. 7. X-ray diffraction pattern of the annealed (900°C for 30 min) $Fe_{28}Ti_{68}Si_4$ alloy. The analysis of the XRD pattern reveals that upon annealing, the equilibrium fcc phase of $FeTi_2$ together with the β-Ti phase (as labeled) is formed.

systems.[7–9] Although the atomic structure of this metastable phase is not known, on the basis of the present investigation and earlier reported results[1–3,17] it may be suggested that the structure of this bcc phase with a large unite cell (~13.15 Å) is expected to contain a periodic packing of Mackay icosahedra, with spaces between them filled with other atoms.[16–18] The packing of Mackay icosahedra in crystalline and icosahedral phases is such that the parallelism of icosahedron is maintained across the phase boundary and consequently, as observed in the present investigation, a coherent orientational relationship exists between them.

It is apparent from the microstructures [Figs. 2(a) and 3(a)] that the *i* phase nucleates and grows from the melt and subsequently undergoes transformation to a metastable bcc phase with a lattice parameter close to 13.15 Å. In our earlier work it was shown that Si substitution impedes the nucleation rate of the icosahedral phase and also suppresses the formation of the equilibrium crystalline phase.[15] It has also been suggested that the quasicrystalline phase in Fe-Ti can form as a product of a eutectic reaction between a liquid and a crystalline phase.[22] The present observation indicates that the icosahedral phase is formed first because of the high nucleation rate arising as a result of topological similarities between the liquid and the icosahedral phase and subsequently the bcc metastable phase starts forming due to the transformation of icosahedral phase during the solidification process.[19] This conclusion is further supported by the observation of the transformation behavior where the icosahedral phase is found to transform to the metastable phase (Fig. 6). These two phases then grow nearly epitaxially leading to built-in orientation relationship between them. Electron-diffraction results suggest that the icosahedral subunits (motifs) remain parallel across the boundary between the crystalline and quasicrystalline phases.

V. CONCLUSIONS

On the basis of the present investigation, it may be concluded that substitution of Fe by 4 at. % of Si in $FeTi_2$ rapidly solidified alloy results in the formation of the icosahedral phase and a metastable bcc phase. The analysis of microstructures and electron-diffraction patterns of the as-quenched and annealed alloy show that the bcc metastable phase with the large unit cell parameter close to 1.31 nm is formed through a transformation of the icosahedral phase. Icosahedral Fe-Ti-Si quasicrystal appears to be a highly disordered phase. This is stable up to a temperature of ~700 °C. The epitaxial growth of the metastable crystalline phase on the icosahedral phase, as found in the present investigation, suggests the similarity of structural subunits present in the two phases. This structural subunit seems to provide the impetus for the formation of the metastable phase.

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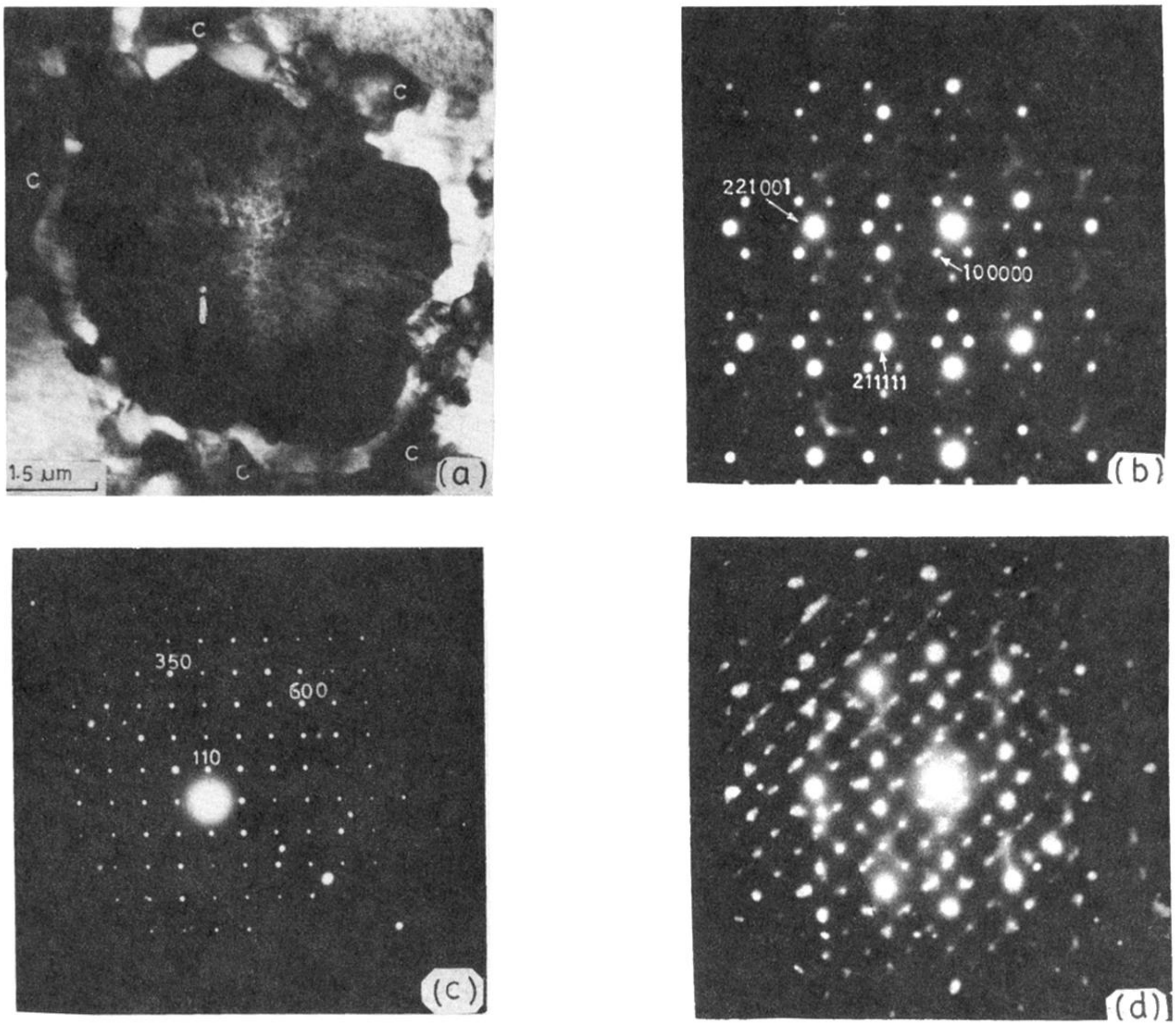
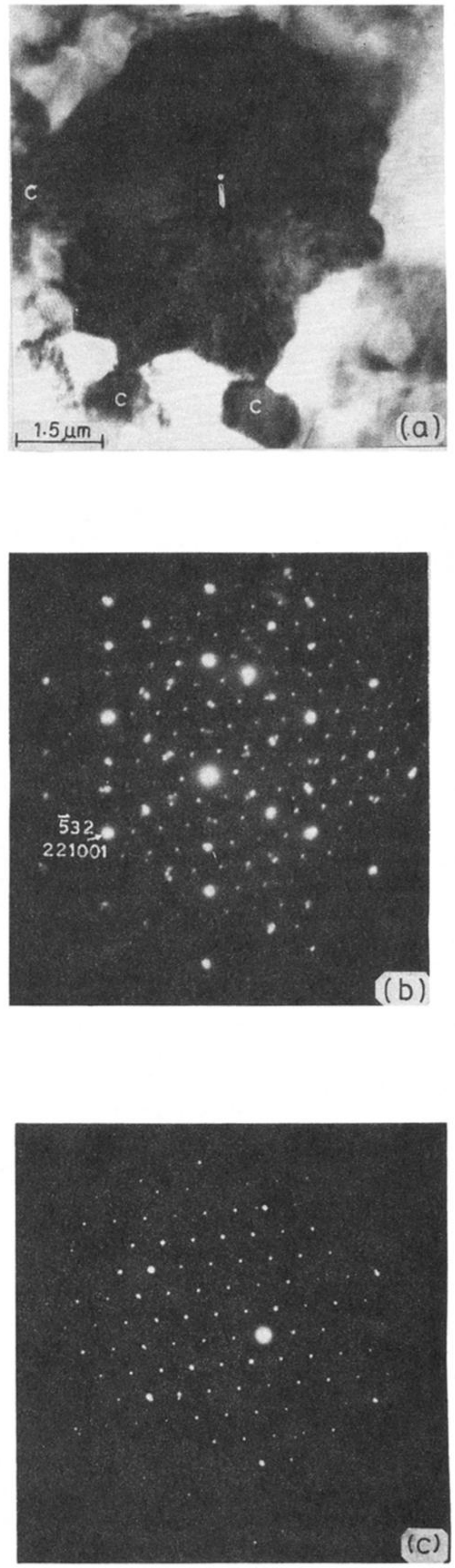


FIG. 2. (a) A representative electron micrograph of as-spun Fe-Ti-Si alloy showing a large roundish icosahedral grain surrounded by a rim of bcc crystalline grains. (b) Selected-area electron diffraction pattern showing twofold symmetry characteristics of the as-quenched *i* phase. Arcs of diffuse scattering can easily be noticed. (c) SAD pattern from ⟨001⟩ zone axis of the metastable bcc phase and (d) SAD pattern showing overlapping of reflections from the icosahedral quasicrystal and the cubic (bcc) crystal.



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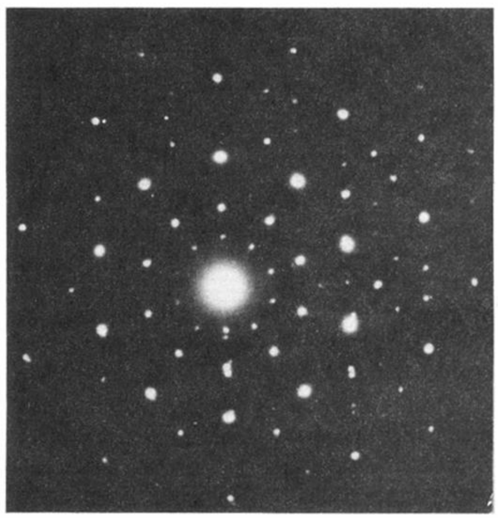

FIG. 4. Fivefold icosahedral pattern with an overlapping ⟨530⟩ cubic pattern.

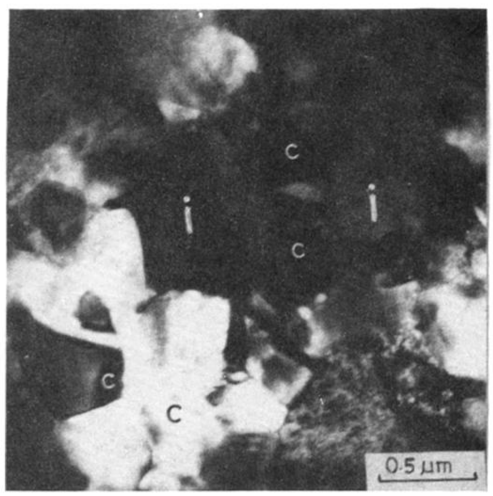

FIG. 6. A representative electron micrograph of the annealed (700°C for 30 min) Fe-Ti-Si alloy showing the larger grain size and increased volume fraction of the metastable bcc phase.