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Commensurate ordering in rapidly solidified Ti-Fe-Si alloys

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We report here the occurrence of a commensurate phase in a rapidly solidified Ti-Fe alloy. On the basis of energy-dispersive x-ray analysis, the composition of the alloy has been analyzed and found to correspond to $Ti_2Fe_{1-x}Si_x$ ($x \simeq 0.03$–0.06), within the limits of experimental error. The x-ray- and electron-diffraction studies have revealed commensurate ordering based on a metastable CsCl-type phase with lattice parameter close to 0.298 nm. Available diffraction evidence suggests that commensuration in this alloy takes place along ⟨100⟩ directions of the basic cell. The ordered cell corresponds to a tetragonal one with cell parameters $a \approx 0.298$ nm and $c \approx 9 \times 0.298$ nm. All the three variants arising due to symmetry breaking of the basic cell have been observed to be related by a threefold symmetry operation. Coherent diffraction of these yields cubic symmetry.

I. INTRODUCTION

After the description of quasicrystalline structures,[1] many scientists have studied the phenomenon of commensurate ordering[2–5] in aluminum–transition metal (M) binary and ternary alloys.[6–8] The similarity of the variation of intensities along the symmetry axis ($\bar{3}$-axis) for the higher approximant phases in these alloys [popularly known as vacancy-ordered τ-phases[8] (VOPs)] has led Chattopadhyay *et al.*[6] to conjecture the existence of a τ_∞ phase in the incommensurate limit in such systems. In these alloys, ordering takes place along [111] direction of a basic CsCl-type structure with $a \simeq 0.298$ nm.[2,3] The competition between the vacancy (V) and the transition metal (M) at the M sublattice site is believed to drive such a commensurate ordering.[3,4] In the process of commensuration along the [111] direction, symmetry is lowered and the cell becomes either trigonal or rhombohedral.[3] The establishment of a link between a row of diffraction spots in icosahedral quasicrystals and VOPs in the incommensurate limit (τ_∞ phase) is based on the electron-diffraction patterns (EDPs) of Al-Cu-Ni alloys[4] which displayed the presence of τ_3, τ_5, τ_8, τ_{13} phases with strong spots lying at the Fibonacci tips (represented by the members of Fibonacci sequence 1,1,2,3,5,8,13,...) along the [111]* row. Numerals appearing in the subscript of VOP designation also follow a Fibonacci sequence. However, it is important to point out here that along with the above Fibonacci VOPs, non-Fibonacci VOPs have also been observed,[8] viz. τ_{18}, τ_{31}, τ_{38}. Noting the similarity of the behavior of (Ti-M)-based binary and ternary allows,[9–13] to that of Al-M with respect to their capability of stabilizing icosahedral and decagonal phases as well as forming hypertwins,[14,15] we were motivated to explore this kind of commensurate ordering in Ti-M alloys. To accomplish that, various compositions of the Ti-Fe alloys under different processing conditions have been studied whose details may be found elsewhere.[16–18]

In the present paper, we report the observation of commensurate ordering in an alloy (without aluminum) with nominal composition of $Ti_2Fe_{1-x}Si_x$ ($0.03 \leq x \leq 0.06$) along ⟨100⟩ direction of a basic CsCl-type structure. Such an ordering leads to symmetry breaking as in the case of VOPs mentioned earlier. However, the resulting ordered structure has been found to be tetragonal, unlike the VOPs of Al-M alloys.

II. EXPERIMENTAL DETAILS

The Ti_2Fe master alloy was synthesized by taking a stoichiometric amount of highly pure constituent elements titanium (99.99%) and iron (99.9%) pressed in the pellet form and melted in a prebaked silica tube under argon atmosphere with the help of rf induction furnace. After initial melting the master alloy ingots were melted again to achieve the complete homogenization. Then it was subjected to energy-dispersive x-ray (EDX) analysis to check the stoichiometry. The EDX analysis shows that besides the presence of titanium and iron there is some incorporation of silicon which might have come from the silica tube during alloy preparation. It has been found that the homogenized alloy ingot does not show the stoichiometric ratio. Instead, an inhomogeneous ternary alloy of composition $Ti_2Fe_{1-x}Si_x$ ($x \simeq 0.03$–0.06) gets synthesized. The thin ribbons of the Ti-Fe-Si alloy (1–2 mm in width and about 40 μm in thickness) were prepared by the melt-spinning technique using a copper wheel of 14 cm in diameter rotating at a speed of about 4200 rpm. The quenching process was conducted in an enclosure filled with argon. The melt-spun ribbons were subjected to x-ray-diffraction analysis using Philips PW-1710 unit with wide angle goniometer. The ribbons were then electrolytically thinned using an electrolyte of 5 vol.% $HClO_4$ in ethanol at -20 °C and examined in a Philips CM-12 electron microscope with a PV-9900 EDX analyzer.

III. RESULTS AND DISCUSSION

Figure 1(a) shows a representative TEM micrograph of the rapidly solidified Ti-Fe-Si alloy. Microstructural observations reveal the development of nodular grains with mottled appearance directly from the liquid. The average

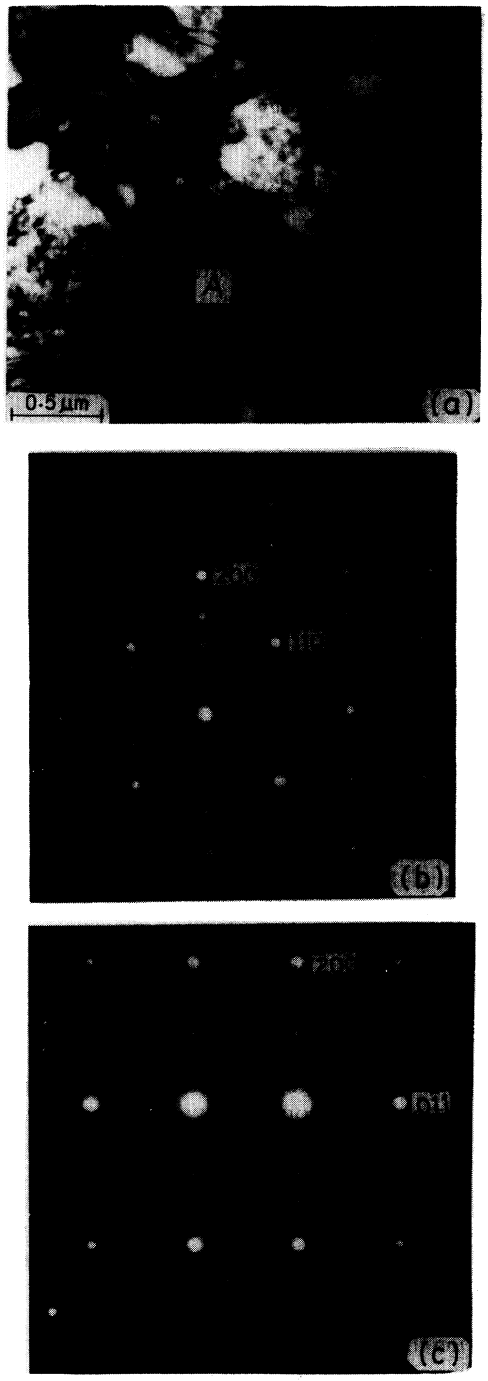

FIG. 1. (a) A representative electron micrograph showing the morphology of the as-quenched $Ti_{69}Fe_{29}Si_2$ alloy. (b), (c) Selected area electron-diffraction patterns from the commensurately modulated phase when the electron beam is parallel to [001] and [011] zone axes, respectively.

composition of the grains has been analyzed by the EDX technique and found to be approximately $Ti_{69}Fe_{29}Si_2$. Figures 1(b) and 1(c) demonstrate the corresponding electron-diffraction patterns (EDPs) from region *A*. Indexing of the main reflections of EDPs has been accomplished based on a CsCl type of cell with a lattice parameter close to 0.298 nm. The known equilibrium phases in this system are face-centered cubic with lattice parameter ~1.13 nm and body-centered cubic with lattice parameter ~0.287 nm for the compositions Ti_2Fe and TiFe, respectively. The detailed structure in regard to the framework of commensurate modulation is being investigated. Indexing and analysis of these patterns reveal many satellite reflections along ⟨200⟩ direction. Observing the diffraction pattern more closely, it has been found that the reciprocal space between transmitted beam and [200]* reflection is divided into 18 parts. It may be pointed out here that due to ordering of a basic cell along the [200]* direction, the first spot is indexable by considering a basic reciprocal-lattice vector $\frac{1}{18}$[200]*, indicating that the cell parameter of the ordered cell along [100] direction is 9×0.298 nm. This ordering obviously leads to a decrease in symmetry and the CsCl-type cell transforms to a tetragonal one.

Figure 2(a) depicts the TEM micrograph with two types of contrast in the nodules. This arises due to the presence of two variants of the transformed ordered tetragonal cell. When these two variants coherently

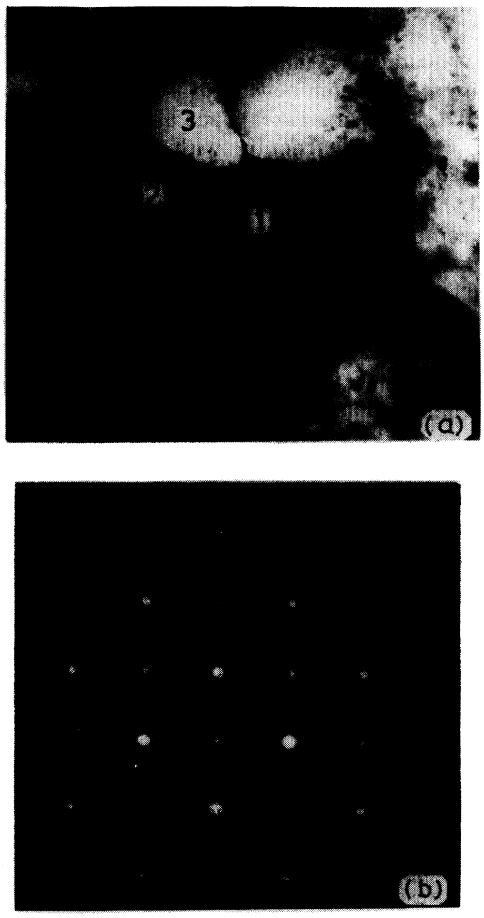

FIG. 2. (a) A representative TEM micrograph depicting different types of contrast in the nodules arising due to the presence of variants (marked 1, 2, and 3) of the ordered tetragonal cell. (b) EDP observed under the [001] zone of variants 1 and 2 of the ordered tetragonal cell.

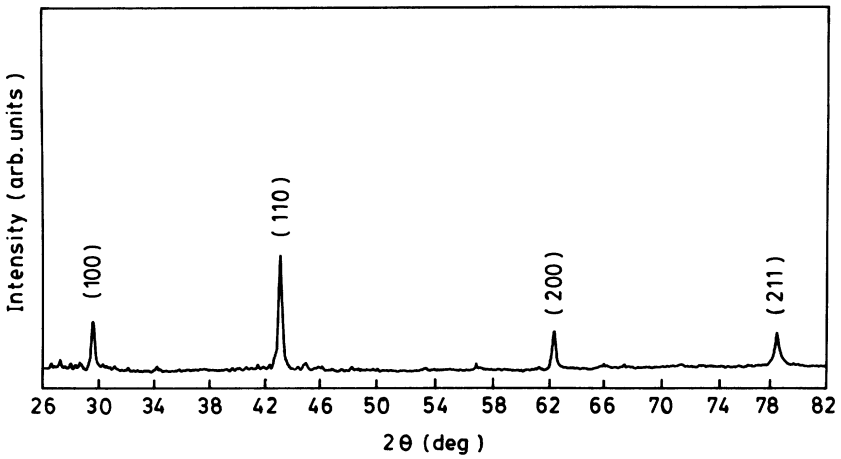

FIG. 3. A representative x-ray powder-diffraction pattern of the rapidly solidified Ti-Fe-Si alloy. Indexing of the x-ray-diffraction peaks has been indicated.

diffract, the result is an electron-diffraction pattern, shown in Fig. 2(b). The two variants [marked as 1 and 2 in Fig. 2(a)] are related by a threefold-symmetry operation around ⟨111⟩ direction of the basic cubic cell. Figure 2(b) is suggestive of the fact that we are dealing with a periodic cubic crystal with commensurate modulation. Apart from the two variants shown above, we do have the presence of a third variant [marked as 3 in Fig. 2(a)] and, consequently, the total number of variants becomes three, which is equal to the index of the $4/m$ point group of order 8 in cubic point group $m\bar{3}$ of order 24.

Figure 3 shows the representative x-ray powder-diffraction pattern of the melt-spun as-synthesized Ti-Fe-Si alloy. Indexing of the x-ray-diffraction pattern reveals that the as-synthesized rapidly solidified alloy corresponds to metastable a CsCl-type phase with lattice parameter $\sim$0.298 nm. This gives support to our electron microscopic observations. Van Tendeloo, Van Heurck, and Amelinckx[8] have shown the commensurate ordering in Al-Cu-Ni VOPs. They have also observed a τ_{18} phase where the strong spot along [111]* direction is divided into 18 parts. However, since the direction of ordering was different than that observed in the present investigation, the explanation put forward earlier[4] about the stability of the alloy may not be totally valid. It is interesting to point out here that the e/a ratio ($\sim$2.05) of the alloys calculated based on Pauling's type of valences approaches close to the typical values of those of Al-M alloys.[19] Therefore, the possibility of vacancies playing a role in stabilizing the present structure may not be ruled out. We also note here that the present alloy manifests commensurate modulation in the presence of Si, whereas the earlier investigations on Al-M-based VOPs (Ref. 8) were devoid of it. The present level of understanding does not permit us to make any firm remark in the Ti-Fe alloy system about the role played by the vacancy and/or silicon, which is a matter for further investigation.

Over and above the commensurate ordering observed in these phases, we also have some secondary features present in them in terms of the diffuse intensity indicating short-range ordering (Fig. 4). This feature is common to almost all the metastable phases produced by rapid solidification where the statistical occupancies of M and vacancies are more important rather than the perfect distribution of transition metal and vacancies at the M sublattice.[4,11]

IV. CONCLUSIONS

In the present investigation, we have shown the phenomenon of commensurate ordering in melt-spun Ti-Fe-Si alloy based on a basic metastable CsCl-type cell with lattice parameter $\sim$0.298 nm. Ordering leads to the symmetry breaking, and the supercell thus formed corresponds to a tetragonal one with lattice parameters $a \simeq 0.298$ nm and $c \simeq 9 \times 0.298$ nm. The tetragonal point group has an index of 3 in the cubic point group. The presence of all three variants have been shown to be related by a threefold-symmetry operation.

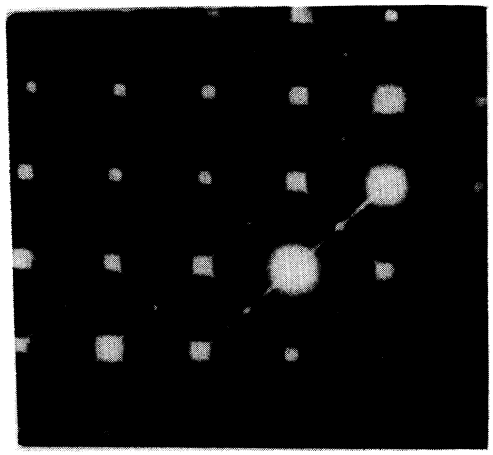

FIG. 4. Selected area electron-diffraction pattern in twofold orientation showing diffuse streaks indicating short-range ordering.

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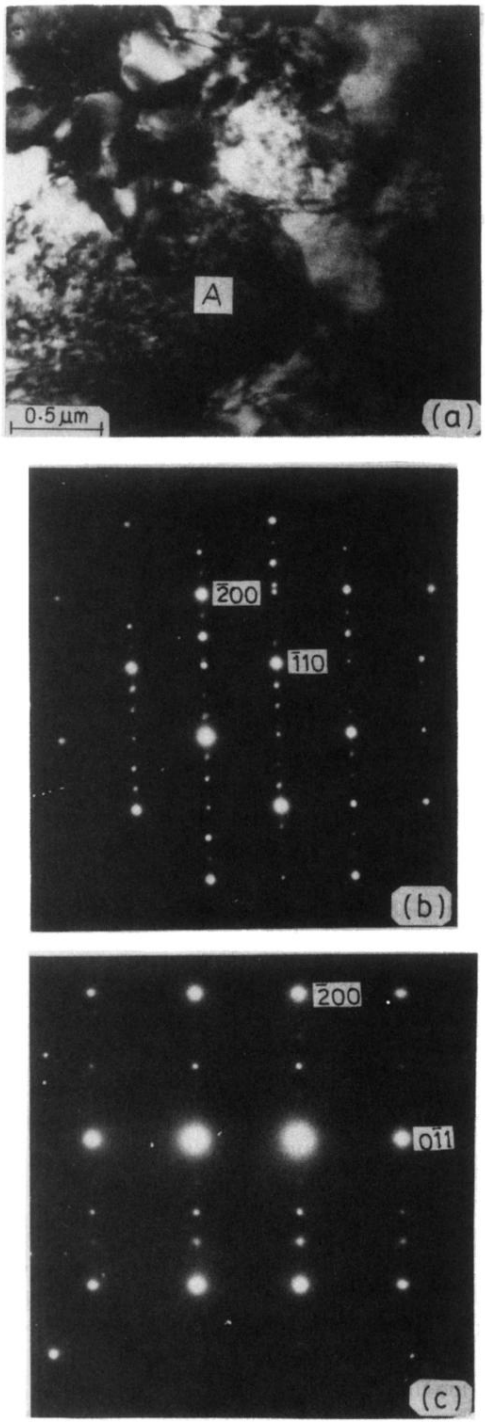

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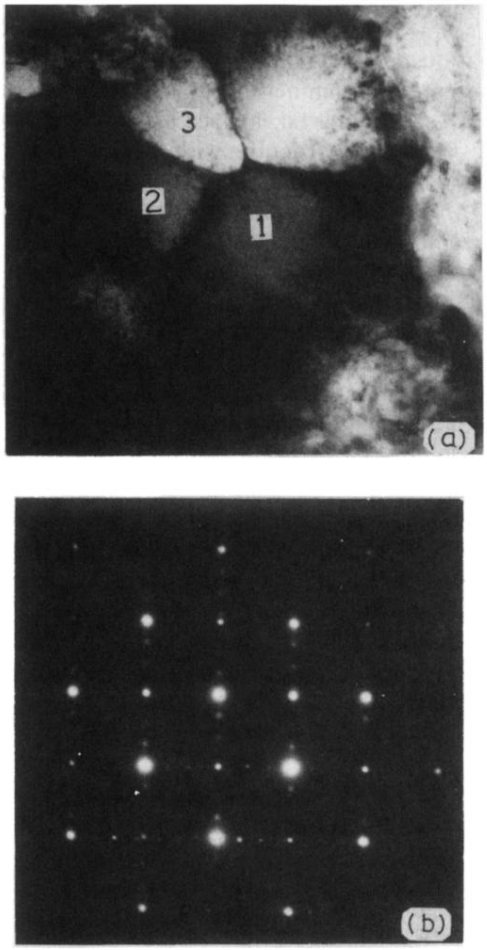

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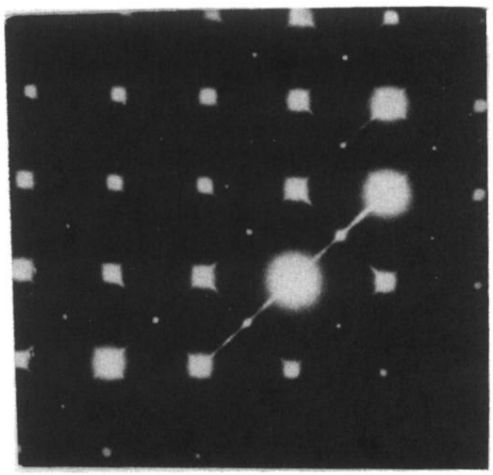

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