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Na-induced Structural Unit in Σ3 [-110]/(-1-11) Grain Boundaries of Si

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The incorporation of impurity atoms at grain boundaries has been suggested to produce changing of interface bonds that result in reduction of material cohesion [1]. Structural studies using HREM taken from a Σ=5[001]/(310) grain boundary of aluminium present in an Al-5% Mg alloys revealed that the incorporation of Mg into the grain boundary alters the structure in some of the basic kite-like structural units of interface and induces such a change in interface bonding [2]. The basic kite-like structural unit of this interface contains seven Al atoms in its structure with one Al atom at the center of the unit. The Mg-incorporated structural unit at the interface contains eight atoms and has two atomic sites made of a coplanar Mg-Mg atom pair at the central atomic site, allowing the unit to be comprised of Al and Mg atoms. Elsewhere [3], calcium segregation at a MgO grain boundary as determined by a combination of atomic-resolution Z-contrast imaging, first-principles density-functional calculations and EELS studies yielded a similar type impurity-induced structural transformation of the interface structure. This paper presents an HREM study that reveals the incorporation of sodium atoms at some Σ3 [-110]/(-1-11) boundaries of Si in a Na-doped Al-12 wt.% Si cast alloy results in structural transformation for the interface structure.

Figure 1a shows a HREM image containing a number of Σ3 [-110]/(-1-11) grain boundaries in a silicon crystal taken from a sodium-doped Al-12 wt.% Si cast alloy. Visual inspection of the image reveals the presence of defect-free (A) and impurity-affected (B) boundaries. Auer electron spectroscopy of the alloy reveals that the Na is mainly adsorbed on (111) surfaces of such twin boundaries Figure 1b is a magnified image of a segment of a defect-free boundary located at A of Figure 1a. The schematic of the orientation relationships of twin projected on the (-110) as drawn from the HREM image of Figure1b is shown as an inset in the image. It should be noted that limited resolution of the 400 keV microscope prohibited the resolution of Si dumb-bells, and the [-110] projected black atomic columns in the images were considered of a FCC crystal. The structure of this segment of the boundary can be described by periodic occurrences of a kite-like structural unit (x) shown as abcd in the inset of Figure 1b containing five atomic columns. The structural unit, also is drawn on the image of Figure 1b, contains only one atomic column at its center and has the width of the CSL. This structural unit is generally considered as correct structural unit of a Σ3 [-110]/(-1-11) boundary of Si. Figure 1c also shows a high magnification view of a segment of the impurity-affected boundary located at B of Figure 1a.The orientation relationships of twin as drawn from the corresponding HREM image is schematically shown in the inset. The boundary in this segment exhibits a periodic arrangement of another kite-like structural, unit (y) shown as efgh in the inset of Figure 1c, but contains six atomic columns. This kite-like unit shows two atomic columns along the direction of electron beam at the center and has the same type of atomic arrangement described for the structural unit x. The two central atomic columns of this structural unit (also drawn on the image of Figure 1c) lay along the length of the twin boundary. Simple comparison of the HREM images of these two kite-like structural units suggests that the center of the y structural unit does not provide sufficient space to occupy two atomic columns of Si dumb-bells. Also based upon similarity in the size of the dark atomic columns that exist at the center of the structural unit y, it seems unlikely that one of the atomic columns belongs to Si and other to Na. It seems to suggest that both atomic columns existing at the center of this unit belong to Na atoms. A literature review revealed that the bonding energy of Na-Na and Si-Si atom pair is 73.60(20) and 326.6(10.0) kJ $mole^{-1}$ respectively [4]. This implies that the structural unit containing lower bonding energy Na atomic pair is expected to experience weaker interaction than that which contains Si-Si atom pair and suggests that the destabilization brought about by the Na-Na pair is weak enough to allow the structural unit y to remain stable at the boundary as observed presently. It is believed that during solidification of the Na doped Al-12 wt.% Si alloys Na atoms of the melt poison the Si growth by incorporating itself into twinned growth tip and retained into the twin boundary as members of an ordered structural unit.

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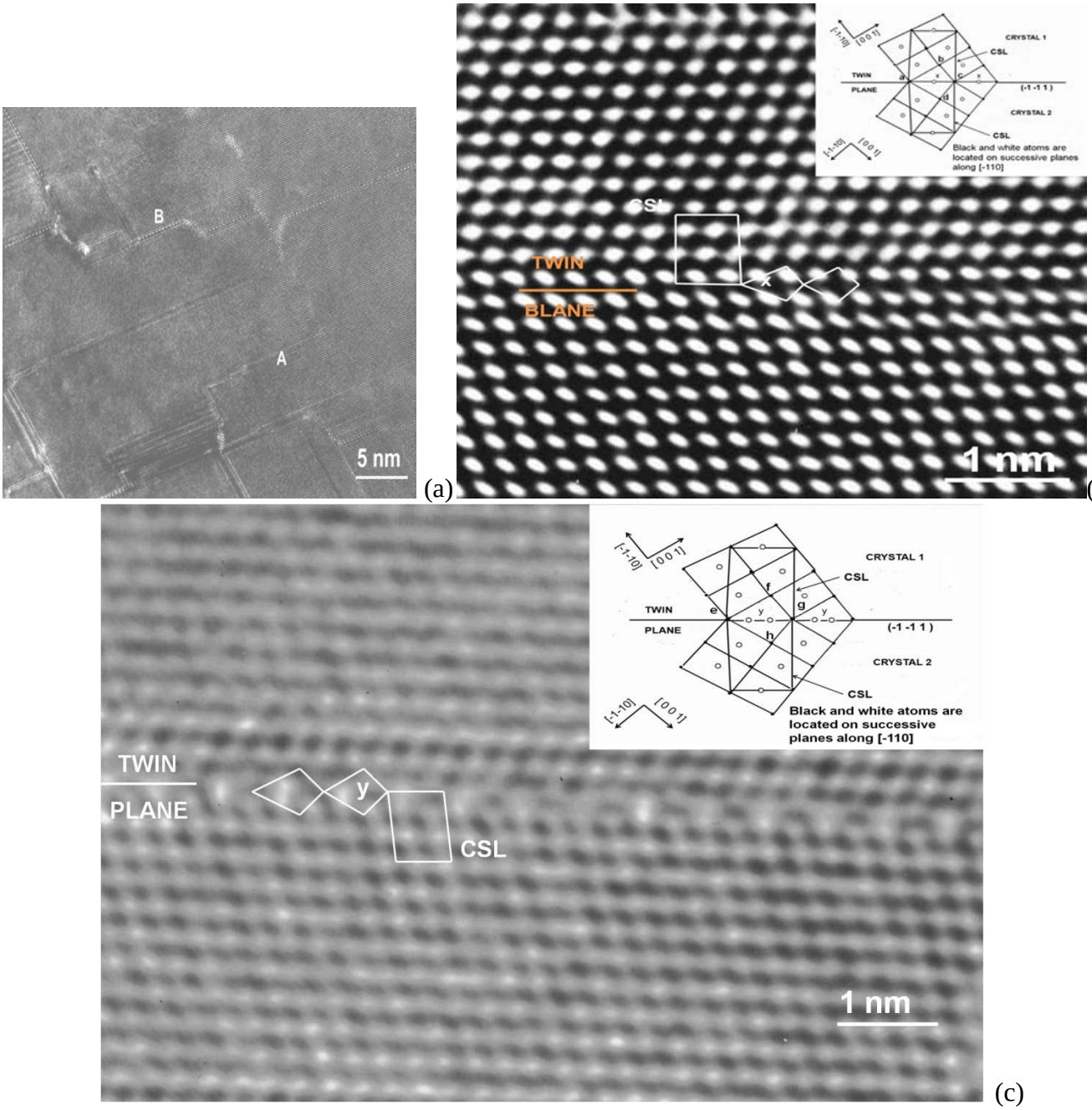

Figure 1: (a) HREM image taken with electron beam parallel to [-110] of a silicon crystal taken from a Na doped Al-12wt.% Si alloy. It exhibits a number of Σ3 boundaries. (b) Magnified image of the location A in (a). A CSL and two structural units (x) are outlined at the twin boundary. (c) Magnified image of the location B in (a). A CSL and two structural units (y) are outlined at the twin boundary.