Letters

On the interaction of annealing twins in f c c metals and alloys

Most f c c metals and alloys of low stacking fault energy develop annealing twins during recrystallization (for example [1]). In many instances, a recrystallized grain will contain twins of a single variant (i.e. twinning only occurs on one {1 1 1} matrix plane), although in certain cases additional variants are also present. Where two or more twin variants are present in any one grain, impingement of the dissimilar twins is possible, in which case a second-order twin is created*. In this short note, the structure of these second-order (Σ9) twins is investigated; primarily in terms of the observation of triangularly prismatic grains in association with the Σ9 grain boundaries. It will be shown that such "twin triangles" are frequently observed in situations where different twin variants impinge and, as has been suggested previously [3], that the twin triangles are stabilized matrix regions.

Four f c c materials have been examined during the course of this investigation, being: (1) pure copper; (2) 70/30 brass; (3) an austenitic stainless steel, and (4) a nickel-base superalloy. Fig. 1a shows a typical micrograph of a recrystallized grain in pure copper. Interaction of the twin slice A with twin B has generated a Σ9 grain boundary C. On closer examination, it was found that part of the Σ9 grain boundary comprised a series of triangular prismatic grains which were twin related to both abutting grains. This was verified by noting that the twin triangles were of the same orientation as the untwinned grain (see the centred dark-field micrograph of Fig. 1b). The observation of twin triangles in association with Σ9 grain boundaries was common to all four alloys. Fig. 2 shows examples of this phenomenon and illustrates the triangularly prismatic morphology generally associated with these grains. The crystallography of these twins is such that they are bounded by two coherent interfaces (i.e. {1 1 1} planes) and one incoherent interface; the latter approximating to a common {1 1 2} plane.

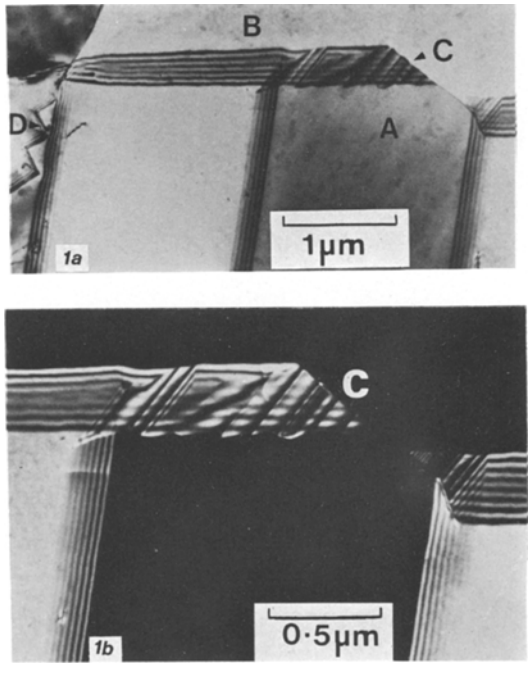

Figure 1 Twin/twin interactions in copper illustrating the formation and structure of Σ9 grain boundaries. (a) A bright field micrograph showing the interaction of two twin variants A and B to form a Σ9 grain boundary (C). A further twin/twin interaction can be seen at D. (b) A matrix dark field micrograph (at higher magnification) showing the occurence of stabilised matrix regions in association with the Σ9 grain boundary (C).

These observations are consistent with those of Vaughan [3] who observed twin triangles in a stainless steel of similar composition to that used in this work, and with the work of Goodhew [4] on specially prepared thin films of gold. However, it would appear that for the systems studied in this investigation, the triangular twins are formed due to the interaction between two primary twins and represent stabilized matrix regions (as in [3]) rather than by the decomposition process, which appears to be occurring in the thin film studies of [4], where it was postulated that a Σ9 grain boundary could dissociate to give a series of triangular grains which were twin related to the

*A second order twin can be considered as a Σ9 grain boundary whereas the primary annealing twin is a Σ3 grain boundary where Σ has the meaning as defined in [2].

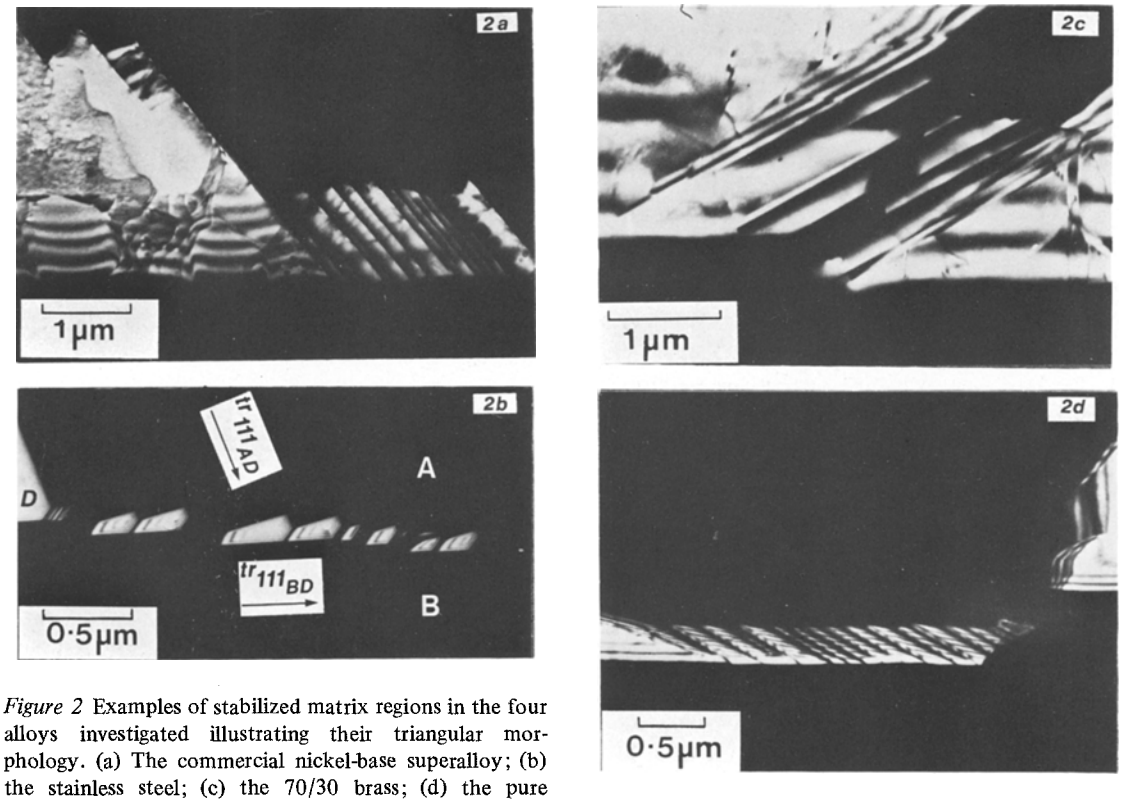

Figure 2 Examples of stabilized matrix regions in the four alloys investigated illustrating their triangular morphology. (a) The commercial nickel-base superalloy; (b) the stainless steel; (c) the 70/30 brass; (d) the pure copper.

abutting Σ9 related grains. The reasons for such a conclusion are as follows:

(1) Twin triangles are nearly always formed when a Σ9 grain boundary is generated by an interactive process; these twin triangles having the same orientation as the original matrix:

(2) Twin triangles are only observed on Σ9 grain boundaries where the interfacial plane approximates to a (1 1 1)/(1 1 4) plane (namely Figs. 1b and 2b); this being consistent with the stability arguments presented in [3].

Although the dominant morphology of the twins associated with the Σ9 boundaries was triangular, other morphologies were occasionally observed. A particular example is shown in Fig. 3, where the impingement of twins A and B has led to the stabilization of a matrix region of complex shape. In this case, the energy argument presented in [4] will have to be modified to include the increased coherent boundary energy associated with the trapezoidal morphology (C).

A further point of relevence to any calculation concerning the energetics of primary twin formation on Σ9 grain boundaries is the contribution due to dislocations which have been observed at the twin/Σ9 triple junctions. Fig. 4 shows an example of the strain field contrast (Fig. 4b) which is associated with these triple junctions (Fig. 4a).

From the observations cited in this short note, it can be concluded that the impingement of dis-

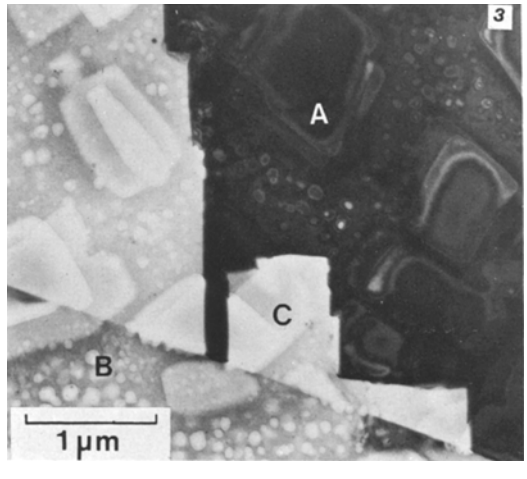

Figure 3 A stabilized matrix region in the nickel-base superalloy exhibiting a complex morphology.

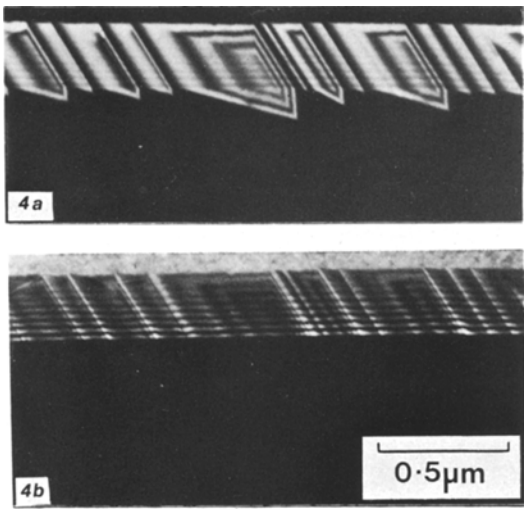

Figure 4 An example of the observation of dislocation-type contrast in association with the stabilized matrix region/Σ9 triple junctions. (a) A matrix dark-field micrograph showing a series of triangularly prismatic matrix regions in association with the Σ9 grain boundary. (b) A twin dark field micrograph showing strain field contrast at the triple junctions.

similar twin variants leads to the stabilization of matrix regions as a series of triangular prisms. In general, these prisms are only observed when one twin variant impinges on the coherent plane of a dissimilar twin variant.

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Vibrational spectra of sulphur-doped borate glasses

One of us has recently pointed out [1] that the blue chromophore in boro-ultramarine should be assigned to the S_3^- ion, and not to S_2^- as suggested by Paul *et al.* [2], but the additional presence of S_2^- was not excluded. The detection of S_2^- in the presence of S_3^- by Raman spectroscopy, has been elegantly demonstrated by Clark and Franks [3] for ultramarine blue. We describe here an investigation of the infra-red and Raman spectra of boro-ultramarine designed to confirm the presence of S_3^- and/or S_2^-. The Raman spectra were obtained using a variety of laser excitation wavelengths and, together with the infra-red spectra, were compared with similar spectra for Reckitt's blue*.

Holzer *et al.* [4] have demonstrated by resonance Raman (RR) spectroscopy of sulphur-doped alkali halides that the stretching frequency of S_2^- occurs at about 590 cm^{-1} and is associated with an optical absorption band at about 400 nm. Similarly, they showed that the totally symmetric stretching vibration of S_3^-, which has C_{2v} symmetry, occurs in the range 523 to 555 cm^{-1} (depending on the host lattice) and is associated with an optical absorption band at about 600 nm. The antisymmetric stretching mode of S_3^- occurs at about 580 cm^{-1} in the infra-red spectrum while S_2^- is, of course, infra-red inactive. RR spectra are obtained when a molecule is excited with a laser line whose frequency falls within the envelope of an allowed electronic transition. Such spectra are characterized by an enhancement in the intensity of a totally symmetric vibration of the scattering molecule and by high intensity overtone progressions.

The Raman spectra were recorded on a Jarrell–Ash model 25-100 double monochromator cali-

*Reckitt's blue was a commercial sample manufactured in England by Reckitt and Son Ltd.