Communication

Rapid Solidification Effects on the Development of an HCP Matrix in a Co-20Cr Alloy

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In the present work, it is experimentally found that rapid solidification enhances significantly the γ-FCC $\rightarrow$ ε-HCP transformation by generating a high density of ε-martensite embryo nucleating defects in a Co-20Cr alloy. Conclusive evidence based on X-ray diffraction determinations combined with SEM and TEM observations indicates that the formation of athermal ε-martensite is strongly influenced by rapid solidification conditions (*i.e.*, up to 89.6 vol pct).

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Co-Cr-Mo-C alloys (ASTM F75) solidified using conventional casting methods retain their high-temperature γ (FCC) matrix structure upon cooling to room temperature. Nevertheless, from the respective equilibrium phase diagrams for these alloys, the stable phase at room temperature should be a fully ε (HCP) matrix. Apparently, the thermodynamic driving force for the γ-FCC $\rightarrow$ ε-HCP transformation is rather small and typically this transformation is rather sluggish with transformed volume fractions of ε-phase of the order of 0.05 to 0.12, in solidified investment casting alloys.[1–4] In addition, the $\gamma \rightarrow \varepsilon$ transformation occurs by a martensitic athermal reaction which is limited by the sparseness of faulting defects which act as effective nucleation sites for ε-martensite embryos. These faulting defects must possess a long range stress field. Among the faulting defects that have been identified are tilt boundaries, twin intersections, incoherent twin boundaries or incoherent inclusion interfaces.[5,6] Apparently, the density of necessary faulting defects for the athermal transformation is strongly influenced by (a) the annealing temperatures and times employed,[7,8] (b) grain size effects[9] and (c) alloy cooling rates.[10–12] The development of potential ε-martensite embryos at the annealing temperatures is controversial,[6,8,13] but there is evidence that increasing the annealing temperatures promotes increasing amounts of athermal ε-martensite upon alloy quenching. However, little or no effort has been made in inducing rapid cooling rates in these alloys. Among the reported works,[10–12,14] it is evident that rapid solidification using atomization or localized surface melting can give rise to over 70 vol pct, athermal ε-martensite, respectively.[15] In this work, rapid solidification in a Co-20pct Cr alloy was achieved by vacuum casting in a wedge-shaped Cu-mold which enabled to attain cooling rates of the order of 230 K/sec in bulk specimens (6 mm width). Under these conditions, the resultant matrix microstructure was almost fully ε-martensite (89.6 vol pct). Figure 1 shows X-ray intensity peaks corresponding to both, γ and ε phases. From this outcome, the amount of ε-martensite was estimated using the expression proposed by Sage and Guillaud.[16] Figure 2 is a scanning electron micrograph showing a high density of martensite plates as identified by the corresponding striations along crystallographic closed packed planes and from plausible nucleating faulting defects. In particular, notice the presence of numerous voids or cavities along prior closed packed FCC planes which are apparently formed by the condensation of excess vacancies. Rapid solidification gives rise to high local vacancy supersaturations which in turn lead to osmotic forces on dislocations.[17] These forces are extremely large and can easily modify the dislocation configuration through various dislocation-vacancy interactions including climbing, the development of dislocation loops and of intrinsic stacking faults (Frank partial dislocations).[17,18] Intrinsic stacking faults have been considered as potential fault defects for the spontaneous nucleation of athermal martensite embryos.[5] Also, since the solidified grain structure is dendritic with no segregation in the interdendritic regions, the ε-martensite striations seem to continue to advance without taking notice of the interdendritic boundaries. In this case, most grain misorientations are expected to be rather small making them highly favorable sites for martensite nucleation, particularly when they can be considered as tilt boundaries. Figure 3 is a transmission electron micrograph showing the presence of γ-Co and ε-Co phases including a diffraction pattern corresponding to γ/ε interface (Figure 3(a)). Also, Figure 3(b) shows a high density of possible embryo nucleating defects such as stacking fault intersections and ε/ε and ε/γ interfaces. Moreover, the development of what seems to be excess vacancies is shown in Figure 3(c). Accordingly, it is evident that rapid solidification promotes the development of an increasing density of potential

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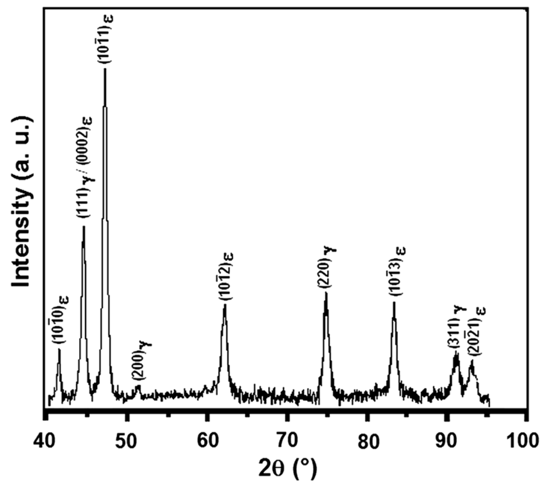

Fig. 1—X-ray diffraction pattern of the directionally solidified as-cast Co-20Cr alloy cooled at 230 K/s.

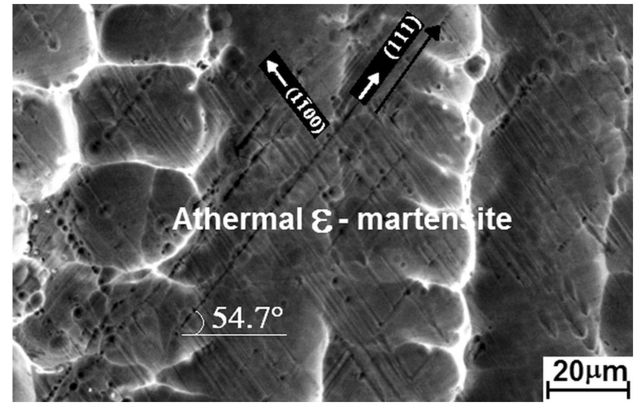

Fig. 2—SEM micrograph showing the as-cast Co-20Cr alloy exhibiting a large density of athermal martensite plates including typical ε-martensite striations within columnar dendrites.

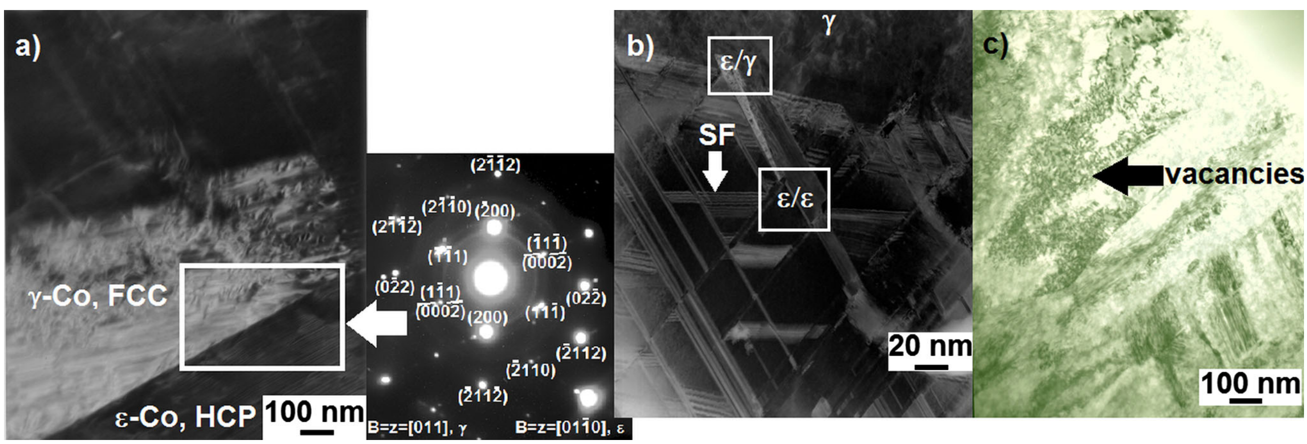

Fig. 3—TEM bright field micrographs of athermal martensite and accompanying defects. (*a*) γ-Co/ε-Co interface and corresponding diffraction pattern, (*b*) a high density of stacking faults, stacking fault intersections and $\varepsilon/\varepsilon - \varepsilon/\gamma$ interfaces and (*c*) a large number of vacancies as a result of rapid solidification.

nucleating faulting defects which strongly favors a γ-FCC $\rightarrow$ ε-HCP transformation. Thus, it is plausible to produce an almost fully HCP matrix in these alloys by implementing high cooling rates through rapid solidification.

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