Rapid solidification of Ni_3Al by Osprey deposition

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A Ni_3Al-based alloy containing Cr is examined after preparation by Osprey deposition. The microstructure consists of solidified spherical regions showing cellular segregation interspersed with regions of finer, equiaxed segregation morphology. The segregation structure is characterized by cell interiors rich in aluminum and poor in chromium, while the cell walls are poor in aluminum and rich in chromium. This segregation pattern is the inverse of that expected, based on earlier melt spinning experience, and is explained in terms of the undercooling of the melt prior to solidification. Very high temperature annealing is required to homogenize the material, despite the use of this rapid solidification process for material fabrication.

I. INTRODUCTION

Considerable attention is devoted at the present time to the development of Ni_3Al-based intermetallic alloys, essentially for high temperature applications. In parallel with these developments, the Osprey spray-deposition process[1] is being considered for the fabrication of such materials which normally suffer from segregation problems when prepared by conventional casting techniques. This note reports the detailed examination of a chromium-modified Ni_3Al alloy prepared by Osprey deposition and in particular examines the extent and characteristics of the segregation microstructure present in this material. Since the spray-deposition process may be regarded as a relatively rapid solidification process, the microstructures obtained will be compared with those found during previous studies of rapid solidification (melt spinning and gas atomization) of similar materials.

Horton and Liu[2] examined the microstructure of melt spun Ni–24 at.% Al, noting that grain interiors contained irregular regions of small antiphase domain size and the remainder, particularly the areas near the grain boundaries, were of larger domain size. This microstructure was explained in terms of the initial dendrites forming during solidification being poor in aluminum, solidifying with a small domain size, while the final liquid to solidify, of composition near stoichiometric Ni_3Al, solidified with a much larger domain size. Cahn[3,4] made similar observations and interpreted the presence of domain boundaries in terms of the off-stoichiometric, aluminum-poor material solidifying initially with a disordered structure, and ordering occurring subsequently by a nucleation and growth process. Very similar results have also been noted by Morris and Morris[5] in Ni_3Al-based alloys modified with chromium and/or iron, although the chemical composition variations between grain interiors and outsides were less important in this study. In a study of gas atomized stoichiometric Ni_3Al, Maurer *et al.*[6] observed equivalent segregation behavior and domain structure, although in this case the first-solidifying material was aluminum-rich since the alloy has a hypereutectic composition: first-solidifying material was the β phase (NiAl) with the finally-solidifying material being substoichiometric Ni_3Al possessing a fine domain size. Very similar results were obtained earlier by Baker *et al.*[7] on near-stoichiometric Ni_3Al. Carro *et al.*[8] have examined melt spun Ni–16.5Al–8Cr, finding a similar dendritic structure and domain size distribution as described above for hypoeutectic material, namely small domains inside the grains and large domains near the grain boundaries in the aluminum-richer areas. On annealing, the domain grew rapidly where the composition was near stoichiometric (grain exteriors) but grew more slowly where the composition was significantly substoichiometric, and there separated into ordered γ' Ni_3Al and thick domain walls of disordered γ. Earlier melt spinning results by Huang *et al.*[9] on stoichiometric Ni_3Al and substoichiometric, chromium containing alloys gave similar results to those described earlier. In particular, in the case of the chromium containing alloys, the grain interiors were poor in aluminum and the grain boundary regions so rich in aluminum that the βNiAl phase formed. Of particular interest in all these studies is that the rapid solidification has not been able to suppress segregation, and initially solidifying material (dendrite centers) is poor in aluminum (or rich in aluminum) for hypoeutectic (or hypereutectic) alloy compositions. The eutectic composition is about 23.5 at.% aluminum for the binary Ni–Al materials.

II. EXPERIMENTAL

The material examined here was obtained from Osprey Metals Ltd. as pieces of a spray-deposited cylinder about 2 cm thick. The material had a nominal composition of 72.0% nickel, 18.1% aluminum, and

8.7% chromium with 0.9% zirconium and 0.3% boron (atomic percentages are used throughout this note) and was prepared by deposition using a nitrogen atomizing gas. The material was examined by optical and transmission electron microscopy in the as-deposited state and also after anneals of 1 h at temperatures above 1000 °C. The foils were prepared by twin jet polishing using a solution of 20% perchloric acid, 15% butoxyethanol, 50% ethanol, and 15% water at −15 °C and 8–10 V and were examined using a Philips CM12 instrument equipped with a Tracor EDS analytical system.

III. RESULTS

Optical examination showed the material to have a uniform, fine microstructure with significant solidification segregation but very little porosity; see Fig. 1. No difference of microstructure was seen between top and bottom regions of the deposited layer, and also no differences between sections with different orientations. Essentially two different morphologies are seen in the optical micrographs, namely approximately circular regions showing a cellular segregation structure radiating from their centers and irregularly shaped regions showing a fine equiaxed morphology. The nearly circular regions, typically about 25 μm in diameter, probably arise from droplets solidifying in flight before deposition onto the growing layer of material. This conclusion is supported by the observation by transmission electron microscopy of widely different orientations from (circular) region to region within the thin foil. The radial structures within each nearly circular region represent thus the cellular or dendritic structure within each solidifying droplet and characterize their rapid solidification. The equiaxed morphology regions show an intensity of mottling which varies from region to region and depends on the degree of etching: the nearly structureless areas seen after mild etching (an example is seen in Fig. 1) take up the equiaxed-etching morphology after more prolonged etching. These regions are believed to arise from the finally-solidifying liquid within the growing deposit.

Figures 2 and 3 illustrate typical microstructures observed by transmission electron microscopy of the spray-deposited material. The cellular segregation mor-

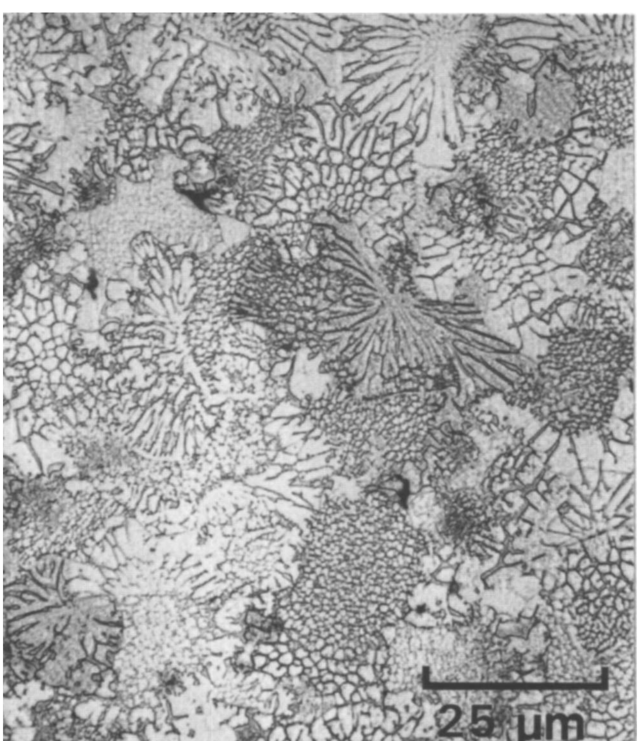

FIG. 1. Optical micrograph showing the uniform, segregated structure of the spray-deposited material.

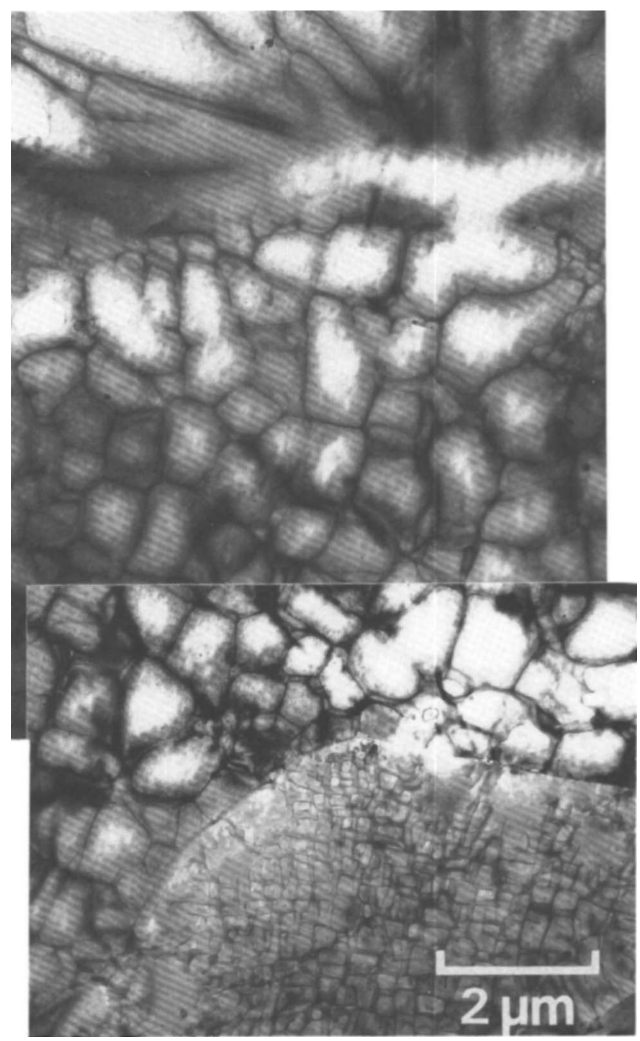

FIG. 2. Montage of transmission electron micrographs showing elongated cellular segregation and equiaxed-morphology segregation in spray-deposited Ni_3Al.

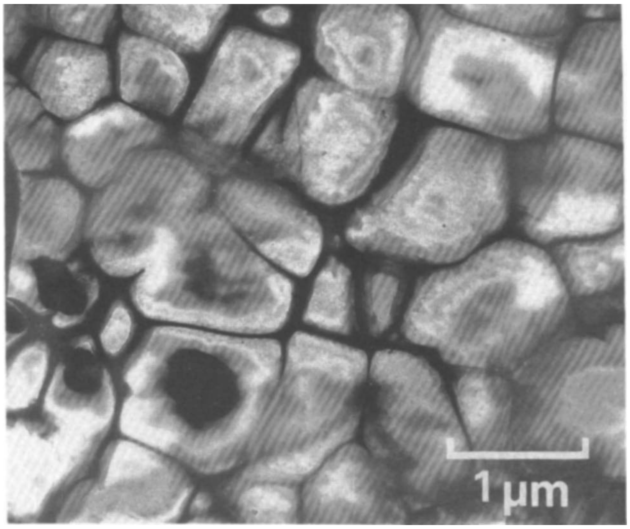

FIG. 3. Transmission electron micrographs illustrating the ordered nature of cell interiors and the disordered nature of cell walls. Dark-field image using a 100 superlattice diffracted beam.

phology can be distinguished, radiating from its center. In addition, part of one of the fine, equiaxed morphology regions can be seen, where the microstructure can in fact be seen to be a very fine, equiaxed cellular segregation structure. Dark-field images taken with several superlattice beams in turn (an example is given in Fig. 3) confirm that the cell centers are ordered Ni_3Al while the cell boundaries always contain disordered material. After considerable growth of the solidification cells, that is toward the outsides of the spherical regions, the cell spacing and cell wall thickness tend to increase. Dark-field imaging of the cell walls here shows these to contain fine speckles, similar to the microstructures seen by Carro *et al.*[8] in annealed materials, and corresponds to the precipitation of ordered γ' Ni_3Al within the disordered regions, presumably occurring as the material cools after deposition. A good example is shown in Fig. 4 for the material after annealing at 1100 °C. EDS analysis of these different regions has been carried out in the TEM using an electron probe of 50–100 nm in size. This is sufficiently fine to analyze the compositions of cell interiors and cell walls, and the results are summarized in Table I. Zirconium was not detected in these analyses in general, but was found within several small particles which were in fact very rich in zircinium (perhaps zirconium borides). Of particular interest in the chemical analyses is the high aluminum content of the cell interiors, in association with a low chromium content. It is re-emphasized here that the alloy examined had a hypoeutectic composition. The high aluminum content was measured identically within all cell interiors, both within the elongated cells and within the equiaxed-morphology cells. Cell walls were conversely very poor in aluminum and correspondingly rich in chromium: the nickel content varied only slightly from cell interior to cell wall. The compositions measured within the speckled cell walls, that is where fine $\gamma' Ni_3Al$ precipitation occurred, were intermediate between the extreme values reported for cell interiors and cell walls; this may be because both cell wall regions and fine γ' precipitates were sampled by the electron probe at the same time.

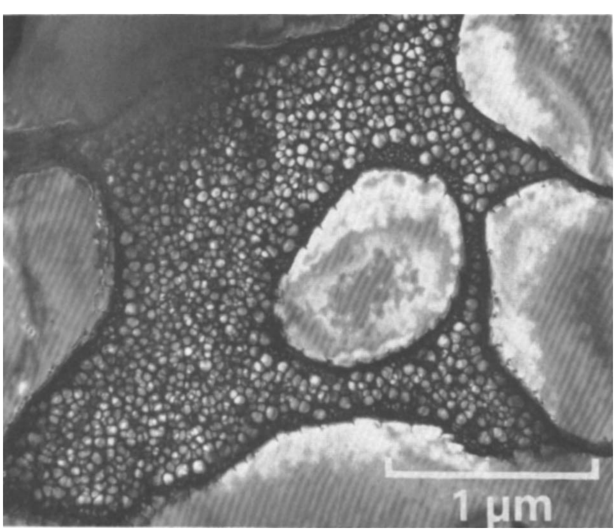

FIG. 4. Transmission electron micrograph showing the fine speckling produced within many cell walls, particularly after annealing. Material annealed 1 h at 1100 °C; dark-field image using 100 superlattice beam.

The microstructure seen after annealing for 1 h at 1100 °C is illustrated in Figs. 4 and 5. The intensity of the contrast caused by the cellular segregation morphology has somewhat diminished, but remains well defined. The cell walls often show fine speckles corresponding to precipitation of ordered Ni_3Al. Table I shows that a certain amount of chemical homogenization has taken place; that is, the chemical composition

TABLE I. Chemical compositions of different parts of the segregated microstructure of deposited and annealed Ni_3Al: EDS measurements (at. %).

	Ni	Al	Cr
As-deposited Ni_3Al			
Cell interiors	70.2	23.4	6.4
Cell walls	73.0	9.0	18.0
Speckled cell walls	72.2	12.0	15.8
Ni_3Al annealed 1 h 1100 °C			
Cell interiors	72.0	22.0	6.0
Cell walls	71.5	11.3	17.2
Speckled cell walls	71.0	12.4	16.6

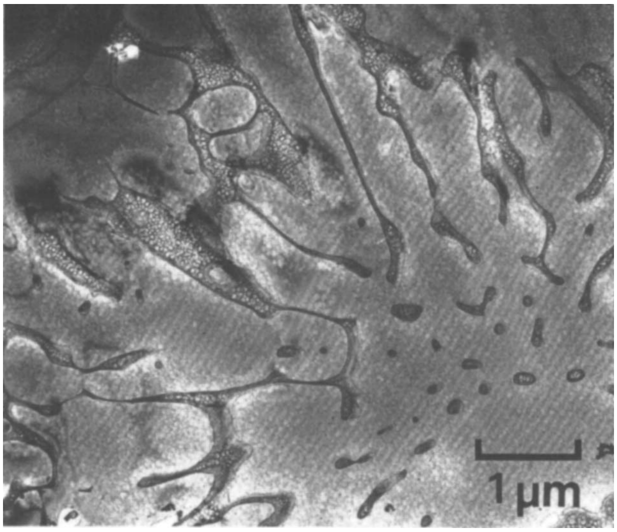

FIG. 5. Transmission electron micrograph showing the remnants of cellular segregation after annealing for 1 h at 1100 °C. Dark-field image using a 100 superlattice beam.

difference between cell centers and cell walls is now smaller, but nevertheless remains considerable. Anneals at 1200–1250 °C for 1 h are required to essentially homogenize this material.

IV. DISCUSSION

The Osprey spray deposition process is believed to show many similarities, in terms of solidification characteristics, to powder atomization techniques. Undercooled droplets are produced by cooling by a gas such that crystal nucleation and growth begins. At a stage when the droplets are partially solid, or perhaps some are solid and others still liquid, impact onto the forming deposit takes place. Solidification is believed to take place rapidly at this stage giving rise to an only slightly porous, and very hot solid. Cooling thereafter takes place very slowly from near the solidus temperature. Certain analogies can be seen with a splat quenching process followed by a very high temperature anneal.

It is not surprising then that the overall morphology seen is similar to that found before on rapidly solidified and heat-treated materials. Carro *et al.*[8] saw disordered domain boundaries, which thickened and showed internal precipitation of ordered Ni_3Al, very similar to the microstructures of Figs. 4 and 5, after rapidly quenching and annealing a hypoeutectic Ni–Al–Cr alloy. These speckled domain walls were also seen here on as-deposited material, as might be expected from the annealing occurring during the slow cool after deposition. In fact, no domain boundaries without associated disordered film were seen here. As shown previously,[3–5] it is those domain boundaries that do not possess a film of disorder that can migrate and anneal out rapidly, while those containing a thicker disordered film require significant chemical diffusion in order to migrate and require much higher temperatures and longer times of annealing.

The most interesting feature here is, however, the observation that the cell interiors, both within the elongated cell regions as well as within the equiaxed-morphology areas, are rich in aluminum and poor in chromium. As emphasized throughout this note, hypoeutectic materials should be expected to show cell or dendrite interiors which are aluminum-poor, as observed in previous melt spinning experiments[2–5,7–9] and as expected from the equilibrium diagram, Fig. 6. The equilibrium diagram of Fig. 6 shows part of the Ni–Al diagram: the present alloy has an aluminum content of 18.1% and is clearly hypoeutectic in composition. A possible explanation of this anomaly involves the influence of undercooling prior to solidification. Examination of Fig. 6 shows that a droplet of the Ni–18.1% Al material undercooled by about 50 °C below the γ liquidus temperature will be below the extrapolated liquidus of γ' and thus has the possibility to solidify by producing directly solid γ', rich in aluminum. The influence of chromium in the alloy on the Ni–Al phase diagram has not been taken into account in this statement: the ternary phase diagram discussed by Huang *et al.*[9] confirms that small additions of chromium do not substantially change the phase relationships or phase fields. According to this argument the cell interiors will probably contain no domain boundaries since solidification may take place directly to the ordered γ' state: the absence of domain boundaries within the cell interiors, as noted here, cannot be used as confirmation of this proposed solidification mode since the high temperature annealing after deposition could well have removed any possible domain boundaries. The implication of the proposed solidification model is, neverthe-

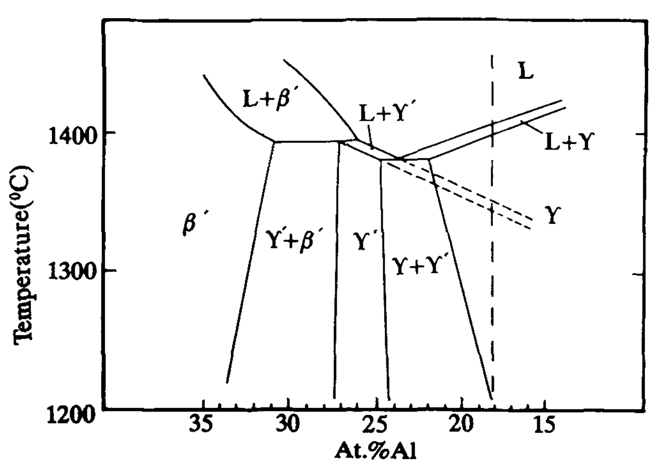

FIG. 6. Part of the equilibrium diagram of Ni–Al showing the region near the $\gamma + \gamma'$ eutectic point. The liquidus and solidus of the L + γ' region are extrapolated into the equilibrium γ phase field.

less, that considerable undercooling of liquid material occurs before solidification, and this, combined with the turbulence due to the impact occurring as solidification takes place, should lead to very fine-scaled microstructures. The high initial degree of undercooling is typical of atomization techniques for solidification and applies to the solidification of the droplets in flight prior to impact and deposition. At this point the grain size of the material will essentially be that of the droplet size, as is typically found during atomization. Previous atomization experiments on Ni_3Al alloys[6,7] have dealt with essentially stoichiometric alloys where the extent of undercooling achieved cannot produce such dramatic changes in microstructure as seen here. Following deposition, the final stages of solidification presumably take place rather slowly, solid state cooling rates are certainly slow for the large and hot deposit, and considerable microstructural changes, even such as recrystallization, may be possible.

V. CONCLUSIONS

A Ni_3Al alloy modified with chromium has been prepared by spray deposition. Even though the alloy is of hypoeutectic composition, the initially solidifying cell interiors are rich in aluminum (and poor in chromium). This unexpected direction of segregation is explained by the significant degree of undercooling achieved prior to solidification, and contrasts with the results of melt spinning experiments on similar alloys. Despite the rapid solidification corresponding to extensive liquid undercooling, and despite the rather fine scale of the microstructure, anneals at temperatures of 1200–1250 °C are required to homogenize this material.

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