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Accuracy of composition measurement using X-ray spectroscopy in precipitate-strengthened alloys: Application to Ni-base superalloys

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Abstract

Large scatters occur in composition measurements using wavelength-dispersive X-ray spectroscopy (WDS) when only a few precipitates are captured in the X-ray sampling volume, because the measured signal represents an averaged composition of the precipitate and the matrix phase in the sampling volume. The scatters become small when sufficient numbers of precipitates are captured and solidification segregation in the sampling volume is not significant. Monte Carlo simulations were carried out to obtain the X-ray signals from the matrix γ and precipitated γ' phases in as-cast Ni-base superalloys using different beam sizes for given γ' precipitate sizes. The optimum beam size in relation to the precipitate size can be predicted for accurate composition measurements.

Keywords: Solidification microstructure; Segregation; Wave-length dispersive X-ray spectroscopy; Nickel alloys; Volume averaging

1. Introduction

Precipitation hardening is the most economical and effective technique used to increase the yield strength of materials, including most structural alloys of aluminium, nickel and titanium. In these alloys, alloying elements are introduced to form intermetallic phases, and fine intermetallic particles can be precipitated to strengthen the alloys. During solidification, most alloying elements partition at the solid/liquid interface, so segregation occurs in as-cast structures during solidification. To achieve high-temperature performance of the alloys, subsequent solution heat treatment is needed to minimize the solidification segregation and thereby to optimize the size, shape and morphology of the intermetallic particles. Therefore, the characterization of solute concentration in as-cast alloys has great importance for control of the final microstructure and properties of the precipitate-hardened alloys.

Single-crystal Ni-base superalloys constitute typical precipitate-hardened alloys. The structure of the superalloys consists of the γ matrix and intermetallic γ' precipitates; the γ-phase is a Ni-base solid solution with a face-centred crystal lattice, while the γ'-phase (Ni3(Al, Ti, etc.)) has an ordered crystalline lattice of type L12. The newer generation Ni-base superalloys contain increasing amounts of refractory alloying elements such as Re, Ta and W [1], which increases the γ' volume fraction in addition to the increased solid-solution strengthening of the γ matrix, thereby improving the high-temperature strength [2–8]. However, owing to the large extent of solidification segregation of these refractory elements, the newer generation Ni-base superalloys form low-melting-point eutectics during solidification and exhibit significant microsegregation in the as-cast microstructure [5,9–15]. This microsegregation and the low melting-point phases need to be subsequently eliminated by a long solution heat treatment at

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elevated temperatures [16–20]. Therefore, it is particularly important to measure solute concentration accurately in the as-cast Ni-base superalloys in order to design and optimize the casting and solution heat treatment processes.

There are several experimental methods for measuring composition in Ni-base alloys. Quantitative electron microprobe analysis (EPMA) using wavelength-dispersive spectroscopy (WDS) is routinely employed [21–30]. EPMA combines the advantages of high accuracy and high spatial resolution, and can be used to collect data from specific areas of the microstructure. A further advantage is that the physics of X-ray generation and propagation through solid materials is well understood, which enables results to be interpreted in detail [31]. The principle of the method is based on comparing the intensity of a characteristic X-ray emission from an element in the specimen with that from a standard of known composition. However, differences exist in the electron scattering, X-ray generation and X-ray emission between the specimen and the standard and therefore '*ZAF*' corrections are applied, where Z denotes the atomic number correction factor, A the absorption correction factor, and F the fluorescence correction factor. The application of the ZAF corrections requires knowledge of the distribution of the generated X-rays as a function of the mass depth, ρz, i.e. $\phi(\rho z)$, where ρ is the density of the materials and z is the depth within the X-ray sampling (interaction) volume [31].

To date, the extent of as-cast microsegregation using EPMA has been assessed using the following methods: (i) series of discrete measurements along a line originating at the dendrite core (first to freeze) to the inter-dendritic (ID) region (last to freeze); i.e. line scans [28–30,32]; (ii) discrete measurements on a large number of points on a square grid overlaid on the microstructure, known as the statistical method [21–27].

In both methods it is assumed that every measured concentration corresponds to a unique fraction solid during solidification and, therefore, any measured difference in composition is deemed to arise from regions freezing at different temperatures (or fraction solid). However, large scatters are always observed in measured composition in Ni-base alloys, even in regions that would have solidified at similar temperatures (or fraction solid). In this study, the implications of the size and distribution of precipitates in Ni-base alloys and the size of the electron beam probe on composition measurements are investigated. A typical third generation superalloy (CMSX10N) was used, and the nominal composition of the alloy is listed in Table 1. CMSX10N has higher refractory additions, such as Ta, W and Re, which are associated with a higher γ' volume fraction (typically 70%) compared with earlier generation alloys. The effect of precipitate size and beam probe size in the sampling volume on concentration measurement is examined using Monte Carlo simulations. The implications of the effect on characterizing microsegregation in Ni-base alloys are quantitatively addressed, and some guidelines are recommended for the analysis of composition measurements.

2. Experimental methods

2.1. Solidification experiments

A fully instrumented industrial directional solidification casting furnace at the Precision Casting Facility, Derby, Rolls-Royce, plc, UK was used to produce single crystal test bars. The test bars have near $\langle 0\,0\,1\rangle$ axial orientations. A complete description of the furnace is available elsewhere [34,35] and only the salient features will be highlighted here. The furnace consists of three zones: (i) a vacuum induction-melting unit; (ii) a resistance-heated central chamber; and (iii) a withdrawal chamber. The basic steps during casting of single crystal seeded components are:

(i) All three zones are evacuated to a partial pressure of 10^{-3} Pa, and the mould cavity, which rests on the water-cooled copper chill plate that is fitted to a ram, is raised into the central chamber. The mould is subsequently left for a period of time (~20 min) to soak.
(ii) Following soaking, the charge in the upper melting chamber is induction melted and poured into the mould cavity. The ram containing the mould is then withdrawn from the furnace at a pre-determined speed. The withdrawal rate in the present experiments was 1×10^{-4} ms^{-1}. The average thermal gradient ahead of the solid/liquid interface was measured to be 3 K mm^{-1}.

Samples for microstructural and compositional characterization were cut orthogonal to the casting axis for microstructural and compositional characterization. The average primary arm spacing was $\lambda_P \approx 300$ μm, and the axial orientation of the primary dendrites was within 8° from $\langle 0\,0\,1\rangle$.

2.2. EPMA

EPMA was carried out using a Cameca SX100 electron probe micro-analyser. All analyses were made using WDS.

Table 1
Composition of bulk CMSX10N superalloy and γ and γ' phases in dendrites [33].

	Ti	Al	Re	Ta	W	Mo	Co	Cr	Ni
Bulk ($\gamma+\gamma'$)	0.1	5.8	6.8	8.4	5.5	0.45	3.1	1.5	68.35
γ	0.06	1.99	16.58	2.34	9.74	0.73	4.95	3.64	59.97
γ'	0.15	6.93	4.7	8.92	6.96	0.34	2.64	1.29	68.07