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Article

Microstructural Evolution of an Intermetallic Phase in a Complex-Concentrated Alloy: a Brief Case Study

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Abstract: In the perspective of designing complex concentrated alloys (CCAs) for structural applications, sigma (σ) phase is important. It is generally known to be an embrittling phase leading to a degradation in the mechanical properties of CCAs. This necessitates detailed investigations on the evolution of σ phase in these alloys. In the present study, an equiatomic CoCrCuMnNi CCA is chosen, in which σ phase appears at 800°C, as reported in a recent publication [1]. To this end, the present investigation aims at understanding the evolution of this phase so that its presence can be controlled for the purpose of preventing degradation in mechanical properties. In the present work, a vacuum arc melted alloy, after homogenisation (at 400°C for 5h), is heat-treated for different times ranging from 1 to 9h at 800°C followed by water quenching. Extensive characterisation has been carried out using X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) techniques to understand the sequence of σ phase precipitation at 800°C.

Keywords: σ phase; high entropy alloy; X-Ray Diffraction; Scanning Electron Microscopy; Transmission Electron Microscopy

1. Introduction

A complex-concentrated alloy (CCA) has been defined to have at least five principal elements, each of which has an atomic concentration between 5% and 35% [2]. These kind of compositions are expected to give high entropy effect and improve the propensity for a multicomponent equiatomic solid solution [3], [4]. This is based on the simple relation: $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$ where ΔG_{mix}, ΔH_{mix} and ΔS_{mix} are the Gibbs free energy, Enthalpy of mixing and the Entropy of mixing [5]. ΔS_{mix} is considered to be equal to the configurational entropy (ΔS_{conf}). $\Delta S_{conf} = k \ln w$ where k is Boltzmann's constant and w is the number of ways of arranging the atoms [6]. When Stirling's approximation is used, the configurational entropy change per mole for the formation of a solid solution from n elements with x_i as mole fraction of ith element (present in CCA) may be expressed as $\Delta S_{conf} = -R \sum X_i \ln X_i$ [7]. $\Delta S_{conf} = R\ln(n)$ where, R is the gas constant (=8.314 J/K mol) [7]. The principal factor which makes the constituent phases of most high-entropy alloys as solid solutions is ΔS_{mix} [8]. Moreover, following Boltzmann's relation between entropy and system complexity, ΔS_{mix} per mole for the formation of a disordered n-element equimolar solid solution, can be expressed as Rln(n) where R is the universal gas constant [5].

The number of phases observed in these CCAs is comparatively less than the maximum number of phases calculated using the Gibbs phase rule, suggesting that large configurational entropy in these alloys enhances the tendency towards formation of solid solutions (chemically disordered or ordered) and thus restricts the formation of intermetallic phases [4]. Furthermore, the diffusivities of atoms (in CCAs) have been reported to be low (or, sluggish) leading to a kinetic constraint on the number of phases which may be formed in such alloys. Thus, the observation of solid solutions in CCAs may not only be attributed to high ΔS_{conf} of these alloys but also to low atomic diffusivities in these multicomponent (or compositionally complex) alloys [9], [10]. These principles have been used in designing CCA microstructures for the purpose of engineering a number of properties required for different applications. On the other hand, σ phase is an intermetallic compound having simple tetragonal structure with space group $P4_2/mnm$ and Pearson symbol tP30 indicating 30 atoms per unit cell [11]. It is generally an AB compound and is responsible for embrittlement in a number of binary systems like Fe-Cr,Fe-V, Co-Cr, Cr-Mn, Co-Mn etc [11]. In CoCrCuMnNi CCA, it is found to be rich in Co, Cr and Mn and forms by mechanism of nucleation and growth between 600^0C -1000^0C [1]. It starts forming at 600^0C and dissolves at 1000^0C, as reported in Refs. [12], [13]. However, till date, there is hardly any report aimed at a systematic understanding on the sequence of precipitation of σ phase in the aforementioned CCA. To this end, the present work is aimed at understanding the evolution of σ phase in CoCrCuMnNi CCA at 800^0C using different characterisation techniques such as X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM).

2. Materials and methods

The equiatomic alloy (with 20 at.% Co, Cr, Cu, Mn and Ni) was synthesized using Vacuum Arc Melting technique (using 99.5% pure Co, Cr, Mn, Ni and Cu). Melting operation was performed four times where every operation consisted of flipping of the solidified mass in order to ensure chemical homogenisation during casting. Casting was subsequently followed by homogenisation treatment at 400°C for 5h followed by slow cooling in a tube furnace. Using electrode discharge machining apparatus (EDM), samples were cut. After vacuum sealing in a quartz tube, samples were heat-treated at 800°C for 1, 3, and 9h (in a tube furnace) followed by water quenching for the purpose of investigating the microstructure as a function of annealing time at 800°C. Using standard metallography techniques (details mentioned in Ref. [15]), the samples were prepared for subsequent microstructural charcterisation.

Phase evolution at different annealing conditions was investigated using XRD (performed between 25 and 80° with a standard scan rate: 0.2°/min and time per step: 20s using Cu K_α radiation with λ= 0.154 nm. XRD-based precision lattice parameters have been determined using Nelson-Riley Method [15]. This is followed by extensive microstructural characterisation using Field Emission (FE) SEM in secondary electron (SE) imaging mode for determining the distribution and morphology of σ phase in individual phases. Chemical composition of individual phases was performed using SEM based Energy Dispersive Spectroscopy (EDS) technique.

For TEM analysis, samples were prepared using the conventional ion-milling route (the details of sample preparation for TEM analysis have been provided in Ref. [16]). Bright-field (BF) imaging using TEM (operated at an accelerating voltage of 200kV) was performed in 800°C, 1h, water quenched condition in order to observe the exact morphology of σ phase evolved in the microstructure. TEM-EDS was subsequently performed to determine the composition of σ phase (in 800°, 1h) which otherwise could not be accurately determined using SEM-EDS technique.

3. Results and discussions

For CCA design, several simple empirical rules are followed which are basically inspired form metallic glass forming criteria and Hume-Rothery rules for solid solutions [5], [17]. Based on quasi-chemical theory (with A and B being atoms of two different species), Enthalpy of mixing (ΔH_{mix}) is the difference between A-B bond energy and combined bond energy of A-A or B-B bonds [2]. It is zero for ideal solutions [18]. $\Delta\mathrm{H}_{\mathrm{mix}} = \sum \Omega_{ij}\mathrm{C}_{\mathrm{i}}\mathrm{C}_{\mathrm{j}}\mathrm{N}_{\mathrm{i}}\ (\mathrm{i} \neq \mathrm{j})$ where Ω_{ij} is the melt interaction parameter determined using Miedema's model, ΔH_{mix} is the Enthalpy of mixing, C_i is the atom fraction of i^{th} element in the alloy [11]. The other parameter which is crucial for CCA design is the atomic size mismatch parameter (**δ**) which quantifies atomic radius mismatch. $\delta = \sqrt{\sum_{i=1}^{N} \mathrm{C}_{\mathrm{i}}(1 - \frac{r_i}{\bar{\mathrm{r}}})}$ where r_i is the atomic radius of i^{th} element and $\bar{r}$ is the average atomic radius determined from

r_i of individual elements using rule of mixtures [10]. On the other hand, valence electron concentration (VEC) has been reported as a useful parameter for determining the formation propensity of intermetallic compounds (IM) (for instance, σ phase in the present work) in CCAs [5]. This parameter is determined from the number of electrons in 4s and 3d orbitals of individual elements, as reported in Ref. [18]. The net VEC of an CCA is calculated from VEC of individual elements (present in CCA) using rule of mixtures. Electronegativity (Δχ) parameter is another important parameter for predicting the possibility of forming solid solution (SS) or IM [3], [19]. $\Delta\chi = \sqrt{\sum_{i=1}^{N} C_i(\chi_i - \bar{\chi})^2}$ where χ_i and $\bar{\chi}$ are the Pauling-scale based electronegativities of the i^{th} element in CCA and average electronegativity of CCA respectively [3]. $\bar{\chi}$ is determined from χ_i using rule of mixtures. In addition, the empirical parameter which shows the relative dominance of the tendency towards formation of disordered solid solution vs the tendency towards ordering or clustering is given as $\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|}$ where T_m is the melting point (in Kelvin scale) for the alloy, determined using Calculation of Phase Diagrams (CALPHAD) based calculations [5]. In the context of σ phases formed in CCAs, paired σ forming element (PSFE) parameter is another parameter which determines the relative tendency towards formation of SS or IM in CCAs based on pairing between σ forming elements [9], [20]. In CoCrCuMnNi CCA, the σ phase forming elements are Co, Cr and Mn as described by Tsai et al. [18]. The empirical parameters determined for CoCrCuMnNi CCA (in the present work) have been tabulated in **Table 1.** Based on **Table. 1,** the parameters which predict the formation of SS are ΔH_{mix}, **δ** and VEC whereas the parameters predicting the formation of IM (for example, σ phase in the present context) are Δχ, *Ω and* PSFE.

Table 1. Empirical parameters for prediction of the relative tendency towards solid solution or intermetallic compound formation in CoCrCuMnNi CCA.

Empirical parameter	**Reported range of formation of intermetallic compound (IM)**	**Value calculated for the present alloy**	**Phases favoured**
Enthalpy of mixing (ΔH_{mix})	<-20 kJ/mol [10], [18]	3.2 kJ/mol	SS
Atomic size mismatch parameter (**δ**)	6.7-8.4 [2]	2.21	SS
Valence electron concentration (VEC)	6.88-7.84 [22]	8.2	SS
Electronegativity (Δχ)	0.09-0.35 [1]	0.145	IM
Ω parameter	<1.1 [3]	0.726	IM
Paired σ forming element (PSFE)	>=40 atom% [7]	40 atom%	IM

4. Conclusions

In the present work, the sequence of precipitation of σ phase (in CoCrCuMnNi CCA) has been investigated at 800°C, with variation of CCAt treatment time from 1 to 9h. The alloy has two major phases viz. FCC2 which is rich in Co and Cr and FCC1 which is rich in Cu and Mn. A mixed morphology of needle-like precipitates (~2.5 µm in length and ~1 µm in width) and globular precipitates (with sizes smaller than the spatial resolution limit of SEM) is observed (in 800°C heat-treated samples) using SEM-based analysis. In TEM analysis of 1h heat-treated sample, along with the needle-like σ precipitates, small (<500 nm) globular σ precipitates are observed. The needle-like precipitates are found to have significantly lower Cr and slightly lower Co-content as compared to that of globular σ precipitates whereas the globular σ precipitates have a significantly lower Cu, Mn and Ni content as compared to that of needle-shaped σ precipitates indicating that morphology of σ phase in CoCrCuMnNi CCA is driven by the compositional heterogeneity between

FCC1 and FCC2 phases. The transition from needle-like σ precipitate (with low Cr and Co content precipitating in Cu- and Mn-rich FCC1 phase) to globular σ containing precipitate (with low Cu, Mn and Ni content precipitating in Co- and Cr-rich FCC2 phase) offers extensive scope for future investigations.

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