JOURNAL OF MATERIALS SCIENCE 26 (1991) 5911–5914

Grain refinement in rapidly solidified W–Si alloys

SOON-GUN KIM, SUNG H. WHANG
Department of Metallurgy and Materials Science, Polytechnic University, Brooklyn, NY 11201, USA

Grain refinement in rapidly solidified W–Si alloys has been investigated with respect to silicon content and solidification rate. Solid-solution W–Si alloys with varying silicon content were prepared into small buttons by arc melting, from which rapidly quenched foils of various thickness were made by the hammer and anvil technique. The grain size of the foils was studied with respect to thickness and silicon content. The results show that the grain size is inversely proportional to the thickness of a foil and also is an exponential function of silicon content on an empirical basis. The combined effect of cooling rate and silicon content on the grain size can be expressed by an exponential function.

1. Introduction

Grain refinement is known as a unique way of enhancing the mechanical properties of metallic materials. By microstructural refinement without causing precipitation, the material can be both strengthened and toughened. This aspect appears particularly attractive in view of the generally observed inverse relationship between strength and toughness. Also, one beneficial effect of grain refinement is revealed by a reduction in the ductile–brittle transition temperature. Grain refinement is mainly achieved by (1) imposing high cooling rates during solidification [1, 2], or (2) alloying dilute grain-refining elements into the base metal [3, 4].

Because of their very high melting points, less attention has been given to rapid solidification of tungsten alloys. Silicon is reportedly identified as a grain refiner in low-carbon steels [4] and Ti–Al alloys [5]. Similarly, a small amount of silicon increases hardness and ductility simultaneously in tungsten alloys, which is accompanied by grain refinement [6]. A quantitative study on the combined effect of rapid solidification and silicon addition on grain refinement has not been attempted previously, especially for the high-melting refractory metals. The objective of this study was to elucidate the relationship between the cooling rate and the grain refinement, with a small amount of silicon addition in the rapidly solidified W–Si alloys.

2. Experimental procedure

High-purity tungsten powders (99.9%) and silicon (99.999%) were mixed in a mortar and cold compacted in a die of 1 cm diameter under 10 000 lbf (1 lbf = 4.4482 N). The cold-compacted pellets were given a surface treatment by an argon arc to facilitate handling. These pellets were then melted and cast into a button about 1 cm diameter and 0.5–0.7 mm thick. Broken pieces (about 0.5 g each) from the button were instantaneously melted and splat quenched into foils 200–500 μm thick and 3–5 mm diameter by the hammer and an anvil technique under an argon atmosphere.

W–Si alloys of various compositions containing 0.15, 0.3, 0.5, 1.0 or 2.0 wt % Si were prepared into splat foils of various thicknesses. Measurements on the grain size of the splat specimens were carried out by optical microscopy and image analysis, but grain sizes smaller than 10 μm were determined by the scanning electron microscopy (SEM). The foils were etched with a solution of 50 vol % HNO_3, 33% H_2O, and 17% HF.

3. Results

Optical micrographs of rapidly solidified W–Si alloys about 500 μm thick are shown in Fig. 1a and b. The grain size in the rapidly solidified tungsten is large (Fig. 1a), typically 100 μm, while it is very small (Fig. 1b) in W–0.5 Si alloy, 10–20 μm. Both micrographs show the matrix as well as the grain boundary being free from precipitates. With increasing silicon concentration beyond the solubility limit (~ 3 at %) a dendritic structure begins to appear and partially cover the matrix as shown in Fig. 2; with 2 wt % Si addition, it became fully dendritic. The grain size is approximately linearly proportional to the splat thickness as shown in Fig. 3, which is consistent with those reported in other rapidly quenched metals [3]. Using the same data, the grain size was plotted against silicon content for the given thickness of the samples as shown in Fig. 4. The correlation line between the grain size and silicon content is not linear, and is concave downward. Also, a systematic shift in the curve occurs with thickness of the samples. It is clearly shown that the grain size decreases exponentially with silicon addition. In particular, a strong refinement with a small amount of silicon is seen in this system.

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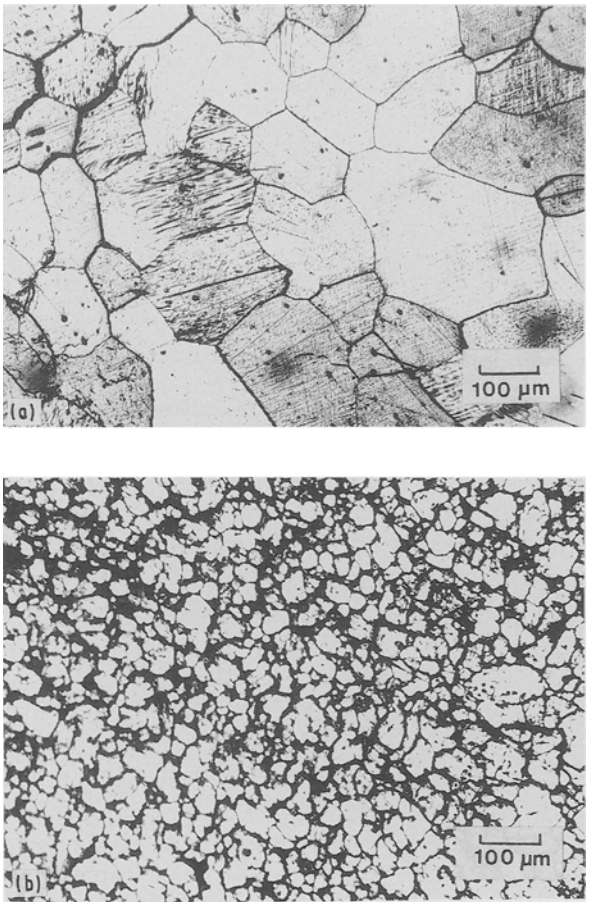

Figure 1 Optical micrographs of rapidly solidified (a) pure tungsten and (b) W–0.5 wt % Si splats, 500 μm thick.

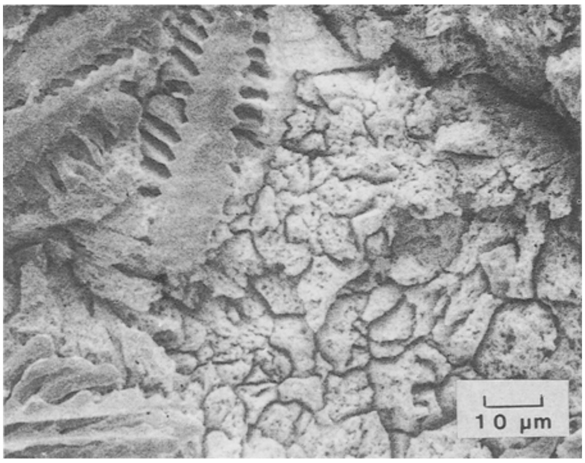

Figure 2 Scanning electron micrograph of rapidly solidified W–1.0Si splat; a dendrite is partially formed.

From Figs 3 and 4 the refinement in this system is seen to be due to the combined effect of cooling rate and silicon addition.

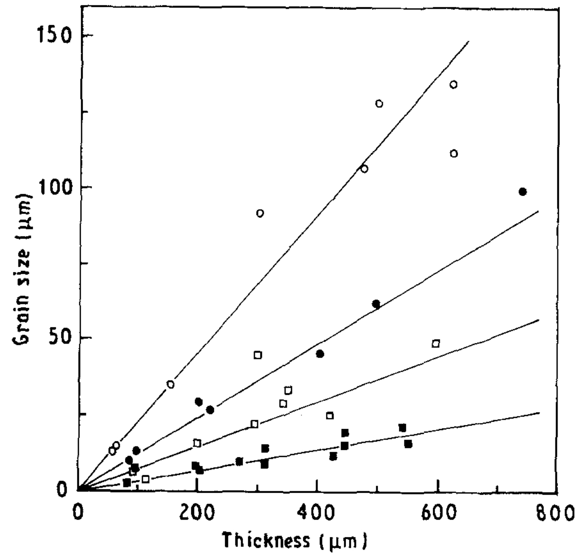

Figure 3 Average grain size versus thickness in W–Si alloys for (○) pure tungsten, (●) W–0.15Si, (□) W–0.3Si, (■) W–0.5Si.

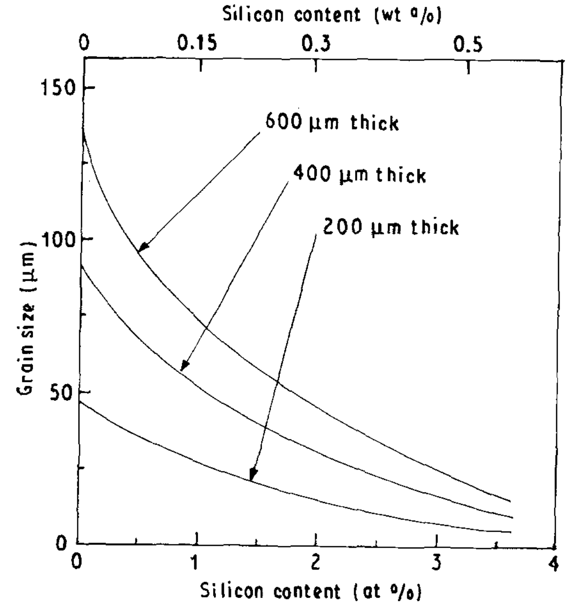

Figure 4 Average grain size versus atomic percentage of silicon in tungsten alloys for various splat thicknesses.

4. Discussion

The cooling-rate dependence of grain size in aluminium alloys was previously investigated by Boswell and Chadwick [7]. From the classical theory of homogeneous steady state nucleation and isotropic linear growth, it was concluded that the average grain diameter, d, is a power function of the initial cooling rate, θ, i.e.

$$d = A\theta^{-n} \quad (1)$$

where A is a material constant assuming nucleation and growth rate are unchanged. Both A and n are sensitive to the magnitude of the free energy required to form a nucleus. The value of n was found to be around 0.9 for aluminium alloys [7].

On the other hand, the cooling rate was found to be inversely proportional to the thickness of rapidly solidified foils, z, under Newtonian cooling conditions, which was theoretically determined by Ruhl [8] using a one-dimensional heat flow model and a finite difference method

$$\theta \propto 1/z \quad (2)$$

Recently, Boderick *et al.* [9] experimentally determined that the average grain size is a power function of the specimen thickness in rapidly quenched Ti–6Al–4V alloys, i.e.

$$d = Bz^m \tag{3}$$

where m was found to be 0.9. Again, B is a material constant which is related to the nucleation and growth variables of the materials. If Equations 1 and 3 are independent of materials and $n = m$, they yield a new relation

$$z = C\theta^{-1} \tag{4}$$

where $C = (A/B)^{1/m}$. The relationship between specimen thickness and cooling rate is in agreement with Ruhl's results [8].

Although the exponent m is 0.9 in Ti–6Al–4V alloy and aluminium alloys, it is difficult to determine from Fig. 3 how much it deviates from the unity in W–Si alloys. It would be more realistic to use unity for the W–Si system, considering the degree of scattering in the d values.

It is clear that this linear relationship is independent of silicon content, as shown in Fig. 3, and precoefficient C in Equation 3 is associated with the silicon content. Fig. 4 shows that an exponential-like relationship exists between the grain size and silicon content for the same thickness of the samples. In Fig. 5, when the log scale of grain size is employed, a linear relationship between grain size and silicon content in the W–Si alloy may be established. This kind of linearity appears to be working in the Al–Zr alloys [10] in which aluminium forms a homogeneous solid solution with zirconium up to 6 at %.

A fair amount of research on the grain-size dependency on cooling rate has been conducted as described before. On the other hand, less attention has been paid in the past to the alloying effect on grain size. In order to understand the nucleation and growth of grains in W–Si alloys, various possible mechanisms are considered here.

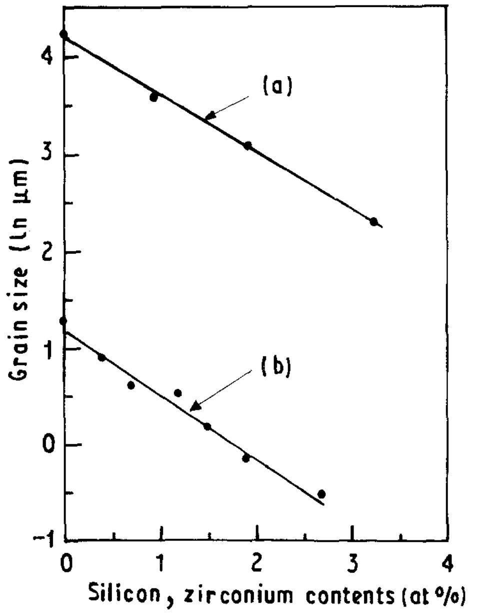

Figure 5 Exponential dependency of grain size on solute contents in (a) rapidly solidified W–Si alloys (300 μm thick) and (b) Al–Zr alloys (~ 50 μm thick) [1].

1. It has been common practice to use inoculating agents added to the melt to produce grain refinement; for example, boron for aluminium alloys, ferrosilicon for cast iron, etc. In these cases, the agent forms a compound through reaction with components of the melt and acts as a heterogeneous catalyst. A grain refinement in Al–Ti alloys (0.01–0.23 wt % Ti) by alloying with small amounts (0.1–0.5 wt %) of silicon and beryllium [3] has been explained by nucleation entropy. It was reported that beryllium was incorporated in a compound $Ti(AlBe)_3$. However, there is no evidence suggesting the existence of any compound in the W–Si alloys studied in these experiments.
2. A small amount of additive causes a peritectic reaction in which the additive solidifies first in a finely divided form and the parent phase nucleates around the agent. An example is zirconium for magnesium alloys. In the case of W–Si alloy, the silicon in the melt neither solidifies first nor constitutes a peritectic reaction.
3. The chemical effect of nucleation and the reduced interfacial tension on alloying [11] are more probable mechanisms for the rapidly solidified W–Si alloys. Turnbull [11] suggested that homophase solute atoms could considerably reduce the undercooling which was required for homogeneous nucleation of a pure metal. When the crystal–melt interfacial tension can be suppressed significantly by foreign atoms, grain refinement will be achieved easily.
4. Measurements of the crystal growth rate in molten tin showed that the rate was reduced by half, with small amounts (0.5 at %) of lead addition [12]. If silicon in tungsten alloys acts in a similar manner, the grain refinement in tungsten alloys will be achieved.

Nucleation and growth theory has been described by exponential functions, which indicates the exponential dependency of grain size on solute content. Because numerous variables in the exponential function of nucleation are unknown in the W–Si alloys, the variables may be conveniently replaced by two empirical terms, i.e. a composition-independent quantity and a composition-dependent one. Based on an empirical approach, a simple empirical relation can be deduced from Fig. 5. Namely, the prefactor C in Equation 4 may be conveniently re-written without knowing A and B

$$C = [\exp - (I_o + kX_{Si})] \tag{5}$$

where I_o is a quantity representing nucleation kinetics of this material, independent of silicon content, k is a constant related to the silicon content, and X_{Si} is the atomic fraction of silicon in the W–Si alloys.

Equations 3 and 5 may be combined to give

$$d = [\exp - (I_o + kX)]z^n \tag{6}$$

In the W–Si system, the constants in Equation 6 can be determined from Figs 3 and 5, where the determined values for I_o, k and n would be 1.46, 59.25 and unity. The empirical relation between grain size, silicon content, and foil thickness in the W–Si alloys may be expressed as

$$d = \exp[-(59.25X_{Si} + 1.46)]z \tag{7}$$

5. Conclusions

The following conclusions can be drawn from the results obtained in this research.

1. A small amount of silicon in a tungsten alloy remarkedly enhances grain refinement.

2. The effect of the cooling rate on grain refinement in the W–Si alloys has been established.

3. The effect of silicon on a tungsten alloy is similar to that of zirconium on an aluminium alloy which forms a complete solid solution in the as-quenched state.

4. An empirical relation describing grain-size dependence on the silicon content and as-quenched foil thickness has been developed.

Acknowledgements

The author acknowledges the support of ARDEC, Picatinny, Dover, NJ, monitored by Dr D. Kapoor, for the rapidly solidified tungsten alloy programme at the Polytechnic University (Contract DAAA21-86-K-0002).

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Received 29 August 1990
and accepted 28 February 1991