Materials Science and Engineering A 403 (2005) 11–16

www.elsevier.com/locate/msea

Purification of chromium by hydrogen plasma-arc zone melting

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Received in revised form 7 March 2005; accepted 27 March 2005

Abstract

Purification of chromium by hydrogen plasma-arc melting (H-PAM) and hydrogen plasma-arc zone melting (H-PZM) has been examined. Especially, reduction of non-metallic impurities, such as oxygen, nitrogen, carbon and sulfur, that have harmful influences on the mechanical properties of chromium, has been investigated. Two kinds of chromium, about 99% (2N-Cr) and 99.99% (4N-Cr) in purity, were used as the starting materials. Remarkable deoxidation, slight denitrogenization and decarburization of chromium were observed in H-PAM, while no reduction of sulfur was observed. Activated hydrogen atoms dissociated in high temperature plasma-arc probably take part in the refining reactions, e.g. deoxidation represented by $\underline{O} + 2H = H_2O$. In addition, it was found that oxygen, nitrogen, carbon and even sulfur concentrations were further reduced at the head side of chromium rods by segregation during H-PZM. Thus, H-PZM with both the segregation effect and the refining effect by H was available to decrease the non-metallic impurities of chromium.

Keywords: Chromium; Plasma-arc melting; Plasma-arc zone melting; Purification; Segregation; Deoxidation; Denitrogenization; Decarburization; Desulfurization

1. Introduction

Chromium has been practically used for plating and as a constituent of alloys with high temperature oxidation resistance and high temperature strength. However, unalloyed chromium is rarely used in massive form because of its brittleness at room temperature. On the other hand, it has been reported that the ductility of chromium increases with increasing purity and very pure chromium is actually ductile [1,2]. The brittleness is recognized not to be inherent but to be caused by impurities, especially by non-metallic impurities, such as oxygen and sulfur [3].

It is difficult, however, to purify chromium due to its high melting point (2163 K = 1890 °C), high vapor pressure (about 1 kPa at its melting point) and strong affinity for non-metallic impurities. Many researchers have endeavored to produce pure chromium through various refining methods. Fusion electrolysis of chromium salts [4], thermal dissociation of chromium iodide [2] and floating zone melting of chromium rod under hydrogen atmosphere [1] have been reported to be effective for the purification of chromium. However, those refining methods and processes are very complicated and of low productivity. The simpler and more practical refining methods for chromium have been required.

In the present work, purification of Cr, particularly for removal of non-metallic impurities, has been investigated using plasma-arc melting (PAM) and plasma-arc zone melting (PZM) techniques developed by the authors.

Plasma-arc melting, which is well known as a useful melting method for various metals and alloys, has been recognized to be efficient for refining and degassing of several metals. When hydrogen is added to the plasma generating gas, we call it hydrogen plasma-arc melting (H-PAM), which has been found to possess excellent refining effects. For example, deoxidation of Fe, Co and Ta [5–7], decarburization of Fe [6] and removal of metallic impurities from Zr, Ta and Fe [8,9] have been reported. These refining effects of H-PAM are thought to be caused by dissociated and activated hydrogen atoms formed in the high temperature plasma-arc.

In addition, the distribution coefficients of oxygen, nitrogen, carbon and sulfur in chromium are estimated to be

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doi:10.1016/j.msea.2005.03.113

Table 1
Impurity concentrations (mass ppm) of electrolytic chromium and high purity chromium used as the starting material

Impurity	Electrolytic Cr (∼99.2%)	High purity Cr (∼99.995%)
O	4000–5000	180–200
N	340–400	50–60
C	∼10	∼7
S	200–220	∼6
Al	<10	11
Ca	–	0.2
Cu	<10	0.02
Fe	900	0.5
Mo	–	0.3
Ni	–	0.1
Pb	30	<0.02
Si	<10	0.2
Ti	–	6
V	–	2
W	–	1
Zr	–	1
RRR	–	180

0.1–0.01, about 0.3, 0.02 and below 0.001, respectively, according to the respective binary chromium alloy phase diagrams [10]. Consequently, it is expected that these non-metallic impurities would be segregated and concentrated to the tail end of chromium rods after zone melting. Then, when hydrogen plasma-arc is used as a heating source of zone melting (H-PZM) for chromium rods, these non-metallic impurities could be further reduced by segregation, in addition to the refining reactions with H. The authors have already examined the purification of metallurgical grade Si (MG-Si) by H-PZM and confirmed the good refining effects for Si [11].

On the other hand, Morvan and Amouroux have reported that a zone melting method with RF-plasma heating was useful for the purification of MG-Si [12]. However, the energy density of RF-plasma flame is much lower than that of plasma-arc and, therefore, RF-plasma is not suitable to a heating source for melting of high melting point materials [13]. So far, purification of refractory metals, such as chromium, by zone melting with RF-plasma heating has not been reported. As compared with RF-plasma, plasma-arc is more useful as a practical heating source for zone melting and, as mentioned above, PZM with hydrogen plasma-arc heating is expected to be effective for the purification of chromium.

In addition, PAM and PZM are operated under atmospheric pressure, so that evaporation loss of the melted metal could be suppressed naturally, unlike vacuum melting method.

2. Experimental details

Two kinds of chromium with different purities, electrolytic one of about 99.2% (2N-Cr) and high purity one of above 99.99% (4N-Cr) as shown in Table 1, were used as starting materials. The total concentration of oxygen, nitrogen, carbon and sulfur in 2N-Cr was as high as about 0.5 mass%, while it was as low as nearly 250 mass ppm in 4N-Cr.

2.1. Plasma-arc melting of Cr

It was examined at first how much of oxygen, nitrogen, carbon and sulfur were removed from the melts of 2N-Cr and 4N-Cr by only PAM with or without hydrogen as a plasma generating gas. The specimen of about 30 g in weight was set on a water-cooled copper crucible with 45 mm in diameter and 4 mm in depth and then melted for 10–60 min by Ar or 10% H_2 + Ar plasma-arc under atmospheric pressure. The power of plasma-arc was set to be approximately 3.6 kW. Pure Ar gas (>99.9995%) and hydrogen gas (>99.9999%) were used as plasma generating gas and introduced into the plasma torch at a flow rate of 5 l/min. More details of the plasma-arc furnace and the melting procedure were described in previous papers [7,8].

2.2. Plasma-arc zone melting of Cr

Fig. 1 shows the schematic diagram of PZM apparatus used in this work. A dc arc discharged type plasma torch with a maximum power of 20 kW is equipped on a stainless steel vessel (200 mm W × 800 mm L × 180 mm H). As a plasma generating gas, pure Ar and H_2 gases were mixed and introduced into the plasma torch at a flow rate of 5 l/min. The specimen rod was placed on the grooved (20 mm W × 200 mm L and 5 mm in depth) water-cooled copper hearth (40 mm W × 240 mm L × 40mm H), which is movable horizontally at a constant speed of 0.1–10 mm/min.

Primary bars of chromium (approximately 25 g of mass, about 15 mm Ø × 40 mm in length) were at first prepared by arc melting under 0.1 MPa Ar atmosphere. Four primary bars were then placed in a row on the copper hearth and zone melted once by Ar plasma-arc to make a Cr rod (approximately 100 g of mass, about 15 mm Ø × 160 mm in length) as a starting material for the following PZM. The power of Ar and 10% H_2 + Ar plasma-arc for PZM was generally set at 3.6 kW and, under the conditions, the length of the molten zone became to be nearly 30 mm. The zoning speed of 3 mm/min was mainly used. The zone-melted rod was turned over after each pass, because the bottom in contact with the copper hearth was not melted. Therefore, the number of passes carried out was an even number from 2 to 10.

2.3. Evaluation of Cr after PAM and PZM

The Cr lumps after PAM were cut out in a given size. The Cr rods after PZM were divided into six equal parts and the center of each part was analyzed for chemical composition. Specimens for analysis were mechanically and electrolytically polished followed by rinsing in acetone and pure water. The oxygen and nitrogen concentrations were determined by the inert gas fusion method using LECO TC-436, and the car-