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Review

Advance in solid-state purification technology for metals

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ABSTRACT

The principle and application of seven purification methods for metals in solid state are investigated. Ultra high vacuum degassing and external gettering can effectively remove interstitial impurities in refractory metals. Interstitial impurity can be decreased to very low level in fused halide salt at low temperature, especially when current flows through. Solid state electro-transport technology can remove both interstitial impurities and many metallic impurities. The application and limitation of solid state thermo-transport technology are also discussed.

Contents

1. Introduction

Recently, high purity and ultra high purity metals are required intensely in high technology industries, i.e., superconductive industry, electric industry and nuclear industry. Thus purification technologies draw wide attention of researchers. Most purification technologies are conducted when metals liquefy or gasify at high temperature, such as vacuum melting and distillation, while purification technologies in solid-state are not given enough attention by researchers.

Melting and distillation in a high vacuum can separate impurities effectively from most active metals [1–3] and transition metals

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[4–8], including rare earth metals [9–12]. These kinds of purification technologies, such as vacuum distillation [13,14], hydrogen plasma arc melting [8] and EB melting [15–18] are relatively clear methods, which can remove most impurities in metals to extremely low levels in ultra high vacuum at high temperature. Zhang et al. [19] obtained 4N5+ pure praseodymium after a two-staged distillation process under vacuum of about 2.0×10^{-4} Pa. Oh et al. [20] purified Ti–Ni alloy by hydrogen plasma arc melting, and the removal degree of metallic impurities exceeded 82% after melting for 20 min. Nevertheless, the mass loss during purification cannot be neglected, especially for volatile metals like some RE metals. Electro-refining technology [21–23] is the most suitable to be applied to non-ferrous metal industry due to its relatively low operation temperature and high productive rate. However, its comprehensive purification capacity is limited by contamination when pure metal atoms deposit on anode. Recently, some novel methods to purify silicon in melting state are developed, such as slag refinement [24], solvent extraction [25–28] and directional solidification [29], however these technologies cannot yet be applied to industrial production due to their complex operation and strict condition requirement.

On the other hand, purification technology in solid state is also a significant part to purify metals, including refractory metals, active metals and even radioactive metals. On the one hand, the theories of solid state purification are academic application and combination of solid state physics, metallurgical physical chemistry, kinetics and electrochemistry. On the other hand, solid state purification technologies are environment friendly and energy saving, and these technologies can be conducted easily in low cost. The main advantage lies in their low treatment temperature (below melting points of metals), while its disadvantage may be the kinetics limitation because of low diffusion or migration rate of impurity atoms in solid-state matrix.

However, nowadays reports about solid-state purification methods for metals are barely rare. Therefore, this paper will discuss seven solid-state purification methods in detail, and further academic research and technical application resulting from this paper are desired.

2. Vacuum degassing

Vacuum degassing technology is usually conducted under high vacuum, and commonly treated to refractory metals of group VB and VIB metals [30,31]. Thus the treating temperature is relatively high to decline the limitation of kinetics though below the metals' melting points. Nonmetallic impurities in refractory metals exist whether in the formation of oxides, nitrides, carbides and hydrides or solutes in the metal lattice [32]. These impurities can be removed by forming volatile suboxide or gas, e.g. N_2, H_2 and CO [33].

Gupta and Bose [30] proposed that deoxidation of refractory metals was conducted in three modes: aluminum deoxidation, carbon deoxidation and sacrificial deoxidation, in means of formation and vaporization of Al_2O, CO and suboxides, respectively. According to Hörz [32], when heated in high vacuum, O, N and C atoms diffused from metal matrix to the metal surface, aggregated and combined to be N_2, O_2 and CO molecules. However, the denitrogenation of vanadium was not feasible by vacuum degassing, at which temperatures and vacuum the vaporization of vanadium was too high [30]. It was proved that carbon could only be removed in formation of carbon monoxide when oxygen was in presence [31,32]. Removal of hydrogen was the easiest among those interstitial impurities. According to Padamsee [34], hydrogen in Nb was removed in formation of H_2, and hydrogen content in Nb could be decreased to below 1 mass ppm by heating at above 1073 K under a pressure of about 10^{-3} Pa.

Ono and Moriyama [35] thermodynamically calculated the potential to deoxidize via volatile oxides of group IVB, VB and VIB metals at temperature near their melting points, and predicted that group IVB metals had the lest possibility to be deoxidized, group VIB metals had the best potential to be purified, and group VB metals had a intermediate tendency. In experimental, oxygen content in niobium decreased from about 1500 mass ppm to several hundred mass ppm after isothermal degassing in vacuum for 0.3 h at 2473 K, and tungsten was deoxidized from 250 mass ppm to about 50 mass ppm after isothermally degassing in vacuum for 2 h at 2273 K. It was also experimentally proved that the presence of carbon in the metals could promote the deoxidation progress.

The kinetics of desorption of oxygen and nitrogen from several refractory metals (V, Nb, Ta, Mo, and W) was investigated by Hörz [32], and the rate-determining steps for each progress were determined. Also the kinetics of decarburization was involved in presence of oxygen under melting point of metals in vacuum, as shown in Table 1.

The vacuum degassing technology is a suitable pretreatment in purifying refractory metals, as the technology can remove a large part of impurity in intermediate good vacuum under low temperature given their high melting points. However, the main drawback of this method may be creep and deformation of large structure because of the gravity, when the treatment temperature approaches the melting points of those refractory metals [34].

3. External gettering

The external gettering technology is an enhanced purification method comparing with vacuum degassing, for the partial pressure of interstitial impurities can be extremely low in presence of getters [36]. When metal samples are in contact to other active materials which have better affinity to interstitial impurities, impurities will transfer from metals to those active materials, and those materials are getters. Getters typically consist of evaporable getters, i.e. magnesium and calcium, and non-evaporable getters, i.e. aluminum, titanium, zirconium, yttrium and silicon. Some gases, such as H_2 [37,38], are also considered to be getters, because when they flow through the surface of metals, some impurities are taken away by forming new substance. This technology is commonly used for refractory metals [31] and also active metals like RE metals.

Table 1
The kinetics of desorption or degassing of oxygen, nitrogen, carbon and hydrogen from V, Nb, Ta, Mo, and W [32].

System	The lowest desorption temperature (K)	Desorption products	Rate-determining step
V–O	1673	VO	Suboxide formation and evaporation
Nb–O, Ta–O	1873	MO, MO_2	
Mo–O, W–O	1273	M_xO_y	
Mo–N, W–N	1873	N_2	Recombination and desorption
Nb–N, Ta–N	1473	N_2	Diffusion
Nb–C–O	1873	CO	
Nb–H	1073	H_2	–