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Journal of Radiation Research and Applied Sciences
journal homepage: http://www.elsevier.com/locate/jrras

Influence of pH and glycine on the K X-ray fluorescence parameters of Zn and Cr in Zn–Cr alloys

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ARTICLE INFO

Article history:
Received 6 March 2014
Received in revised form
24 March 2014
Accepted 25 March 2014
Available online 5 April 2014

Keywords:
Cross-sections
K X-ray intensity ratios
Charge transfer
Zn–Cr alloys
pH and glycine

ABSTRACT

In this study, $\sigma_{K\alpha,\beta}$ production cross-sections and K_β/K_α, intensity ratios of Cr and Zn have been measured in pure metals and in different alloy compositions which have different composition values. The alloying effects on the fluorescence parameters of Cr and Zn were investigated and the changes in these parameters interpreted according to the rearrangement of valance state electrons and the charge transfer process between the 3d elements which constitute the alloys. The samples were excited by 59.5 keV γ-rays from a ^{241}Am annular radioactive source. K X-rays emitted by samples were counted by an Ultra-LEGe detector with a resolution of 150 eV at 5.9 keV. The effect of pH and glycine values on alloy composition and alloying effect on the K x-ray fluorescence parameters of Cr and Zn were also investigated.

1. Introduction

The increasing application of alloys in various fields such as industry, agriculture, archaeology, etc. requires accurate knowledge of X-ray fluorescence parameters. In addition, comparison of measured K X-ray fluorescence cross-sections with theoretical estimates provides a check on validity of various physical parameters such as photoionization cross-section and fluorescence yields.

A great deal of investigation has been performed on experimental and theoretical K X-ray fluorescence parameters of 3d transition metals. Earlier theoretical values of fluorescence yield were obtained in the region $4 \leq Z \leq 54$ by McGuire (1969, 1970) and Walters and Bhalla (1971) using the Hartree–Fock–Slater model. Cu K x-ray production cross

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Peer review under responsibility of The Egyptian Society of Radiation Sciences and Applications

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.jrras.2014.03.004

sections for 1.7-MeV/amu C, N, O, and F ions were determined in the limit of vanishingly thin solid Cu targets. The inclusion of electron transfer from the target K shell to the projectile in addition to direct ionization of the target in order to explain the charge-state and Z_1 dependences of the X-ray-production cross sections (Gardener et al., 1979). Kahoul, Abassi, Deghfel, and Nekkab (2011) calculated empirical K-shell fluorescence yields (ω_K) from the available experimental data for elements with $6 \leq Z \leq 99$. The experimental data are fitted using the quantity. There have been extensive experimental investigations on K_β/K_α X-ray intensity ratios and fluorescence yields of 3d transition elements (Be, Lepy, Plagnard, & Duchemin, 1998; Benall, Shidling, & Badiger, 2005; Brunner, Nagel, Hartmann, & Arndt, 1982; Casnati, Tartari, Baraldi, & Napoli, 1985; Çevik, Kaya, Ertugral, Baltas, & Karabıdak, 2007; Şimşek, Doğan, Turgut, & Ertuğral, 2000).

The binding energy of the valence electrons of an element, incorporated in different alloys has different values due to the change in the valence electrons participating in the formation of the chemical bond. As a result transition probabilities of a valance electron leading the variations in the K X-ray fluorescence parameters (Kalaycı et al., 2005). K_β/K_α X-ray intensity ratios of V and Ni in V_xNi_{1-x} alloys have been measured following excitation by 59.54 keV γ-rays from a 200 mCi ^{241}Am point-source. The experimental data indicate deviations of K_β/K_α intensity ratios for V and Ni in certain alloy compositions from the corresponding ratios for pure metals. These deviations indicate that the relative changes of the number of 3d electrons for V and Ni seem to be very similar if considered as functions of their own concentrations (Raj, Padhi, & Polasik, 1999). In Zn_xCo_{1-x} alloys (Aylıkcı et al., 2011), reduction the polarization depend on the changing the pH values of electrolyte. As a result of this dependence concentration of alloy composition is changed and this behavior causes an alloying effect on the K X-ray fluorescence parameters.

The change on the 3d electron population of both elements in different alloy composition is known to be alloying effect on the K X-ray fluorescence parameters. 3d electron population in the atom has a serious effect on the 3p orbitals more than the 2p orbitals which results in a change of the K_β/K_α X-ray intensity ratios. Because 3d and 4s levels are the valence state of 3d transition metals. These shells are far away from the nucleus respect to the inner shells (2p orbitals). Outer shells feel the attract force of nucleus more weakly than 2p orbitals and so alien element affect the valance shell more than inner shells. Therefore it can be said that K X-ray fluorescence parameters are a sensitive tool to investigate the electronic structure of 3d transition metals in alloys, compounds and complexes. Influence of the alloying effect on the K_β/K_α X-ray intensity ratios were investigated for Ti, Cr and Ni in Ti_xNi_{1-x} and Cr_xNi_{1-x} alloys (Bhuinya & Padhi, 1992), Fe and Ni in Fe_xNi_{1-x} alloys (Raj, Padhi, Polasik, Pawlowski, & Basa, 2000), Ti, Cr, Fe and Co in their alloys (Pawlowski et al., 2002). The changes between the experimental and theoretically values of elements constitutes the alloys can be explained by assuming rearrangement of electrons between 3d and (4s, 4p) valence band states of the individual metal atoms. In addition to these studies, the alloying effect on the K shell fluorescence yield was investigated for Cr, Ni and Al elements in Cr_xNi_{1-x} and Cr_xAl_{1-x} alloys (Büyükkasap, 1998). Raj, Padhi, Polasik, Pawlowski, and Basa (2001) irradiated the Fe_xNi_{1-x} alloys due to the rapid advance of magnetoelectronics. Valance electronic structure of Fe and Ni in Fe–Ni alloys calculated using the results obtained from K_β/K_α X-ray intensity ratios. K and L shell X-ray fluorescence parameters of Co, Cu and Ag in pure metals and different alloy compositions were determined using EDXRF by Aylıkcı et al. (2009). $\sigma_{L\beta}$, $\sigma_{L\alpha}$ of Ag and $\sigma_{K\beta}$, $\sigma_{K\alpha}$ of Co and Cu X-ray production cross sections values compared with theoretical values. It was explained the alloying effect using the changes on the X-ray florescence parameters. For the Cr, Zr, Nb, V, W, Mo and Al elements, the alloying effect on the trend of elastic properties of TiN-based nitrides have been investigated using ab initio density functional theory calculations within the generalized gradient approximation (Chen, Zhao, Rodgers, & Tse, 2003). The valence-electron structure of Ti and Co in the Ti_xCo_{1-x} were calculated by the comparison of the measured *Kα*-to-*Kβ* x-ray intensity ratios with the results of multiconfiguration Dirac–Fock calculations for various electron structures of these metals (Han & Demir, 2010).

In this paper, Zn and Cr elements in the different alloy composition were measured by the EDXRF system. The $\sigma_{K\beta}$ production cross-sections and K_β/K_α X-ray intensity ratios of these elements in Zn_xCr_{1-x} alloys was investigated and the obtained values were interpreted according to the rearrangement process of the valance state.

2. Experimental procedure

2.1. *Electrodeposition of Zn–Cr alloys*

$Zn_{1-x}Cr_x$ alloys have been electrodeposited with an approximate thickness of 2 μm on aluminum foils from chloride baths at room temperature. The working electrodes were aluminum foils and AISI 4140 steel disks. All these electrolytes were prepared from Merck pro-analysis grade chemicals using double-distilled water and consisted of $ZnCl_2$ 67.5 gl^{-1}, N_2HCH_2COOH 200 gl^{-1}, H_3BO_3 31.5 gl^{-1}, NH_4Cl 95.4 gl^{-1}, $CrCl_3 \cdot 6H_2O$ 160 gl^{-1} for the Zn–Cr alloys (Table 1).

The measured quantity for the pH and glycine was adjusted according to Table 1. The plating time was 15 min, after which the cathode was withdrawn, washed with distilled water and dried. The deposition potential was −1.5 V.

Before electrodeposition, aluminum foils were mechanically polished with silicon carbide emery paper, degreased in 1 M NaOH with surfactant at 70 °C during 5 min and finally rinsed with the twice distilled water (18 MΩ cm) and dried in air. Counter electrode was a Pt electrode, for the polarization and the corrosion measurements. The reference electrode used in all experiments was a saturated calomel electrode (SCE). All the potentials are referred against SCE. The electrodeposition of alloys was performed with an electrochemical analyzer/workstation (Model 1100, CH Instruments USA) with a three-electrode configuration realized at room temperature in a Pyrex glass cell. The exposed area of the specimens was about 1 cm^2 (Doğan et al., 2013). The agreement of lattice parameters with reported values confirms that films are hexagonal and polycrystalline.