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Cluster formula of Fe-containing Monel alloys with high corrosion-resistance

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ABSTRACT

The cluster-plus-glue-atom model is applied in the composition interpretation of Monel alloys. This model considers ideal atomic nearest neighbor configurations among the constituent elements and has been used in understanding compositions of complex alloys like quasicrystals, amorphous alloys, and cupronickels. According to this model, any structure can be expressed by cluster formula [cluster](glue atom)$_x$, x denoting the number of glue atoms matching one cluster. According to this model, two groups of experimental composition series $[Fe_1Ni_{12}]Cu_x$ and $[Fe_yNi_{12}]Cu_5$ were designed which fell close to conventional Fe-containing Monel alloys. The designed alloys after solution treatment plus water quenching, are monolithic FCC Ni-based solid solutions. Among them, the $[Fe_1Ni_{12}]Cu_5$ alloy has the highest corrosion resistance in simulated sea water, and its performance is superior to that of industrial Monel 400 alloy.

1. Introduction

Monel alloys are based on Ni-rich Ni–Cu alloys containing approximately 30 wt.% copper [1,2]. They are highly corrosion-resistant in sea water, acidic and alkaline media, and in many oxidizing and reducing gas environments [3,4]. Industrial applications of Monel alloys were started by the International Nickel Company of Canada for vessels, pipelines, and valves, and later were found in wide fields ranging from huge naval leviathans to tiny electronic components [5–8]. However, in high Cl^- concentration environment they suffer from severe pitting corrosion [9], which needs further optimization of chemical compositions.

Apart from the base elements Ni and the major element Cu, other minor elements are also present. For instance, the most popular Monel 400 (Chinese standard NCu28–2.5–1.5) has a relatively simple composition with Ni 63.0–70.0, Fe≤2.50, Mn≤2, Si≤0.50, C≤0.30, S≤0.024, Cu=balance (wt.%). This is an FCC single-phase alloy without precipitation strengthening. Among the alloying elements, the minor elements Si, C, and S are not introduced specifically as alloying elements so that the basic composition involves four elements Ni, Cu, Fe, and Mn. Ni and Cu form the base, and the minor alloying elements Fe and Mn are from raw materials but also contribute favorably to the corrosion resistance. Then the composition interpretation concerns the determination of the relative contents of Cu with respect to Ni and the total amount of Fe plus Mn. However, it is noted that in the industrial standards the compositions vary over a range and the composition control replies on empirical standards imposed by suppliers and end users. Considering the presence of multiple elements, the element optimization is hard to reach experimentally and suitable alloy design principles should be introduced for such a purpose.

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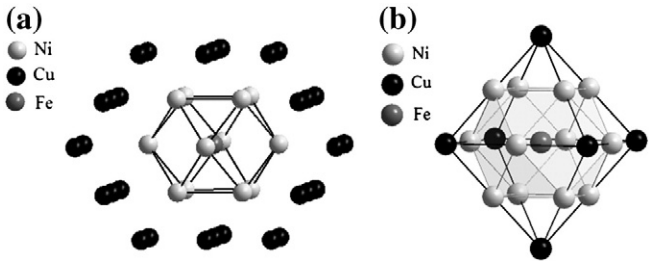

Fig. 1 – Cluster-plus-glue-atom models for Cu–Ni–Fe FCC solid solution alloys conforming to cluster formulae $[FeNi_{12}]Cu_x$ (a) and for Monel alloys where the glue atoms are the six 2nd-shell atoms Cu (b).

The key issue here is the stability of a solid solution containing sufficient amounts of solutes necessary for given functions, i.e. the formability of a single-phase alloy in a conventional heat treatment scheme that contains the maximum amount of solutes. Many solid-solution-based alloys are actually compromises between the structural destabilization by solute alloying and the demand for maximum amounts of the solutes for desired functions. For instance, typical austenite stainless steels require Cr as the main corrosion-resisting alloying element but Cr is a ferrite stabilized element and it will severely destabilize austenite, thus Ni has to be introduced for the austenite stabilization.

The solution to this problem lies in the structural model for stable solid solutions. Any stable solid solution should satisfy the nearest neighbor configurations as required by the chemical interactions of the constituent elements. In studying the composition rule of Cu–Ni-based and Fe-containing cupronickel alloys, we have developed a method termed cluster-plus-glue-atom model that originated from quasicrystalline and amorphous alloys [10]. The atomic size differences of Cu, Ni, and Fe are negligibly small so that any chemical effect can be easily manifested as resulted from enthalpies of mixing. A relatively large and positive enthalpy of mixing between Cu and Fe ($\Delta H_{Cu-Fe}=13$ kJ/mol [11]) indicates that Cu is immiscible with Fe. Fe and Ni exhibit a small negative enthalpy of mixing $\Delta H_{Fe-Ni}=-2$ kJ/mol [9] and tend to be nearest-neighbored upon alloying. Cu and Ni atoms show a small positive enthalpy of mixing ($\Delta H_{Cu-Ni}=4$ kJ/mol [11]), so they can form a solid solution at high temperature. Based on these simple assumptions, we have established a stable solid solution model for Cu-rich cupronickels as shown in Fig. 1(a) [12], where one solute Fe is surrounded by twelve Ni atoms to form an $FeNi_{12}$ cuboctahedral cluster, which is then embedded in a Cu matrix, and the resultant alloys are described by a cluster formula $[Fe_1Ni_{12}]Cu_x$. Such a model avoids Cu–Fe nearest neighbor and allows the maximum Fe–Ni and Cu–Ni nearest neighbors. It was proven by experiments that the Fe/Ni=1/12 alloys indeed showed the best corrosion resistance [12], but the optimized Cu content relative to the amount of the $FeNi_{12}$ clusters was not solved.

Using the same cluster-plus-glue-atom model formulated as $[Fe_1Ni_{12}]Cu_x$, here in this paper, Monel alloy compositions are explained and optimized with regard to their corrosion resistance.

2. Cluster-plus-glue-atom Model for Monel Alloys

Let us examine the composition feature of the most popular Monel 400 with Ni 63.0–70.0, Fe≤2.50, Mn≤2, Si≤0.50, C≤0.30, S≤0.024, Cu balance (wt.%). Disregarding the minor non-alloying elements Si, C, and S, choosing the two extreme compositions Ni63 and Ni70, and taking the maximum Fe and Mn contents, we obtain two basic compositions expressed in atomic percent $Ni_{64.9}Cu_{30.2}Fe_{2.7}Mn_{2.2}$ and $Ni_{71.8}Cu_{23.4}Fe_{2.7}Mn_{2.2}$ (at.%). In the following, atomic percent or fraction is used unless specified. These two compositions are transformed into the model cluster formula as $[(Fe_{0.5}Mn_{0.4})Ni_{12}]Cu_{5.6}$ and $[(Fe_{0.5}Mn_{0.4})Ni_{12}]Cu_{3.9}$, where the number of Ni is set as 12 in order to satisfy the requirement of the cuboctahedral cluster in the cluster-plus-glue-atom model. Immediately we can see

Table 1 – Designed compositions according to composition formulae $[Fe_1Ni_{12}]Cu_x$ and $[Fe_yNi_{12}]Cu_5$, and their corrosion parameters in a 3.5 wt.% NaCl solution.

No.	Alloy compositions		Cluster formula	E_{corr} (V) vs SCE	I_{corr} ($\mu A/cm^2$)	E_b (V) vs SCE
	at.%	wt.%				
1	$Ni_{80.0}Cu_{13.3}Fe_{6.7}$	$Ni_{79.4}Cu_{14.3}Fe_{6.3}$	$[Fe_1Ni_{12}]Cu_2$	−0.350	2.550	−0.011
2	$Ni_{70.6}Cu_{23.5}Fe_{5.9}$	$Ni_{69.4}Cu_{25.1}Fe_{5.5}$	$[Fe_1Ni_{12}]Cu_4$	−0.395	4.583	0.034
3(8)	$Ni_{66.7}Cu_{27.8}Fe_{5.5}$	$Ni_{65.3}Cu_{29.5}Fe_{5.2}$	$[Fe_1Ni_{12}]Cu_5$	−0.216	0.791	0.089
4	$Ni_{63.1}Cu_{31.6}Fe_{5.3}$	$Ni_{61.7}Cu_{33.4}Fe_{4.9}$	$[Fe_1Ni_{12}]Cu_6$	−0.371	6.583	0.057
5	$Ni_{57.1}Cu_{38.1}Fe_{4.8}$	$Ni_{55.5}Cu_{40.1}Fe_{4.4}$	$[Fe_1Ni_{12}]Cu_8$	−0.351	8.614	0.020
6	$Ni_{68.6}Cu_{28.6}Fe_{2.8}$	$Ni_{67.1}Cu_{30.3}Fe_{2.6}$	$[Fe_{0.5}Ni_{12}]Cu_5$	−0.303	2.499	0.129
7	$Ni_{67.6}Cu_{28.2}Fe_{4.2}$	$Ni_{66.2}Cu_{29.9}Fe_{3.9}$	$[Fe_{0.75}Ni_{12}]Cu_5$	−0.325	1.987	0.024
8(3)	$Ni_{66.7}Cu_{27.8}Fe_{5.5}$	$Ni_{65.3}Cu_{29.5}Fe_{5.2}$	$[Fe_1Ni_{12}]Cu_5$	−0.216	0.791	0.089
9	$Ni_{65.8}Cu_{27.4}Fe_{6.8}$	$Ni_{64.5}Cu_{29.1}Fe_{6.4}$	$[Fe_{1.25}Ni_{12}]Cu_5$	−0.291	1.028	0.028
10	$Ni_{64.9}Cu_{27.0}Fe_{8.1}$	$Ni_{63.7}Cu_{28.7}Fe_{7.6}$	$[Fe_{1.5}Ni_{12}]Cu_5$	−0.332	2.660	0.048