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Effect of Ni to Cu Ratio on Formation of Oxide Scale at High Temperature

Shrikant Jadhav[1*], Prashant Date[2] and Rajkumar Singh[1]

[1]Kalyani Centre for Technology and Innovation, Bharat Forge Ltd., Pune, Maharashtra, India

[2]IIT Bombay, Powai, Mumbai, Maharashtra, India

[*]**Corresponding author:** Shrikant Jadhav, Kalyani Centre for Technology and Innovation, Bharat Forge Ltd Pune 411036, Maharashtra, India, Tel: 020-67042777; E-mail: Shrikant.Jadhav@bharatforge.com

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Abstract

Metals, which are especially used in the hot forging applications, are stable, when exposed to the atmosphere, at high and low temperatures. Metals such as iron, rusts and get oxidised very rapidly, while the other metals such as nickel, chromium corrode relatively slowly. Therefore it is important to study oxidation process along with film thickness of the oxide layer. The role of various alloying elements and its oxides during oxidation process need to be understood. Copper strongly influences the microstructure of micro alloyed steel since segregation of Cu occurs in steel during oxidation. Samples containing various Ni/Cu ratios are studied in SEM and XRD. Four samples of ratio of 1.8, 2.0, 2.5 and 5.0 with dimension size 25 mm × 25 mm are studied. The sample which has ratio of 1.8 gives better results since it shows minimal severity in cracking and optimum thickness is achieved.

Keywords: Oxide scale; Ni to Cu ratio; XRD; SEM; Oxide scale thickness

Introduction

Use of recycled scrap in manufacturing industries becomes necessity for the sake of recycling and this leads to degradation in quality of steel. Residual or tramp alloying element such as Ni, Cu, S are difficult to remove during production of steel [1].

This mechanism is termed as hot shortness. In the hot shortness phenomena, Copper oxidizes rapidly than Fe at high temperature and enriches at scale/metal interface. When Cu exceeds its solubility range in austenite, a liquid Cu penetrates into austenite grain boundaries and causes cracking during forging [1].

Nickel causes surface defects on the steel. As small as 0.1% Ni causes iron oxide on the surface of steel [1]. Copper and nickel element in the surface of the steel during hot rolling causes surface defects. Therefore, it is important to understand and control the behavior of the distribution of these elements.

Alloying Nickel is beneficial for special purpose since Ni increases the scale adherence with low free oxygen. Ni containing steel when exposed at high temperature contains two types of scale, i.e., inner scale and outer scale.

But, after air cooling some part of outer scale spalls off and inner scale remains intact with steel surface which increases 3% to 5% adherence of scale [2]. However during manufacturing process scale which is formed on steel during reheating is hard to remove. Most of times steel has tendency to form different oxide layers at high temperature.

The thickness of these layers goes on increasing at high temperature which then degrades the quality of final product. Similarly, on other hand Cu also plays an important role in corrosion resistance along with little adverse effect on steel surface such as cracking of surface at high temperature [3].

Copper causes serious problems such as cracking of steel surface during forging and rolling. Copper also segregates to MnS inclusion exacerbating the problem of segregation [4]. Nickel has tendency to enrich near scale metal interface [5]. It is also known that copper precipitates in the steel as CuS precipitate which reduces the ductility [6].

Recent works have reported that combine addition of Copper and Nickel encourages the grain coarsening in micro alloyed steel. However the addition of Nickel has been reported as most important, because it increases the solubility limit of copper in austenite to surpass the problem of surface cracking [6].

Thus the effect of Cu and Ni on the surface cracking of steel at high temperature with oxidation has been investigated. Moreover microstructure and composition of phases formed at scale/metal interface were investigated. Therefore, this study is related to various Ni/Cu ratio at high temperature in detail. This paper investigates the composition of phases formed on steel, and effect of Ni/Cu ratio on scale adherence. This study also reveals the optimum Ni/Cu ratio in the micro alloyed steel [7].

Experimental Details

Steel with four different ratios of Ni/Cu were cut to size of 25×25 mm taken for the study. The chemical composition are shown in **Table 1**

Table 1 Chemical composition of micro alloyed steel (mass %).

Ni/Cu	C	Mn	Si	P	S	Cr	Ni	Cu	V	Ti
5	0.39	1.6	0.7	0.35	0.05	0.2	0.1	0.02	0.13	0.035
2.5	0.33	1.52	0.5	0.2	0.023	0.19	0.05	0.02	0.1	0.01
2	0.38	1.5	0.52	0.14	0.04	0.22	0.08	0.04	0.23	0.009
1.8	0.34	1.62	0.45	0.15	0.02	0.12	0.09	0.05	0.033	0.033

These four samples of steel were taken for oxidation study. Heat treatment were carried out on all samples. The samples were heated at 115°C in an atmosphere of 2% O_2 +12% H_2O with 1 hr soaking time followed by air cooling. After heat treatment on the samples, scale formed during air cooling was collected for further examination. Microstructure at scale/ metal interface after oxidation were observed using Scanning electron probe micro analysis (SEM), energy dispersive spectrometer (EDAX). Samples were taken for X-ray diffraction (XRD) for the phase analysis.

Results and Discussion

A cross sectional SEM image of steel with four different ratios of Ni/Cu after oxidation has been studied. The SEM images of scale metal interface in the various Ni/Cu ratio of micro alloyed steel oxidized at 1150°C are shown in the **Figure 1**. As metallic phase were occlude into scale, the interface became uneven and cracking took place as result of presence of high Ni/Cu ratio. Internal oxidation also occurred in the fracture surface.

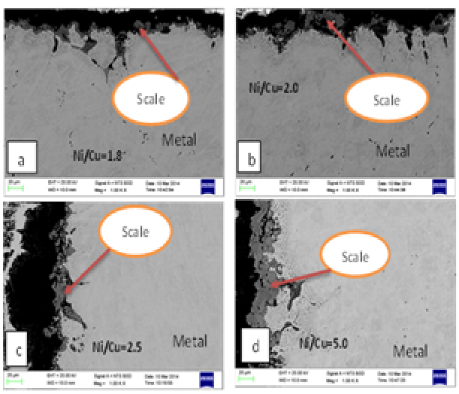

Figure 1 Scale metal interface of steel of various Ni/Cu ratio at high temperature.

Thickness and unevenness of oxide scale formed on the surface of steel containing Ni/Cu ratio 5 is higher as shown in **Figure 2**. It has been found that oxidation takes place exactly at inner/outer scale metal interface where porosity and cracking is more sever. It has been concluded that severity of cracking is more when ratio is more as the result of oxidation. Spectrums processing in **Table 2** shows total 100% and standard element detected are as follows to form different oxides in the scale such as iron oxide chromium oxide, nickel and copper oxides.

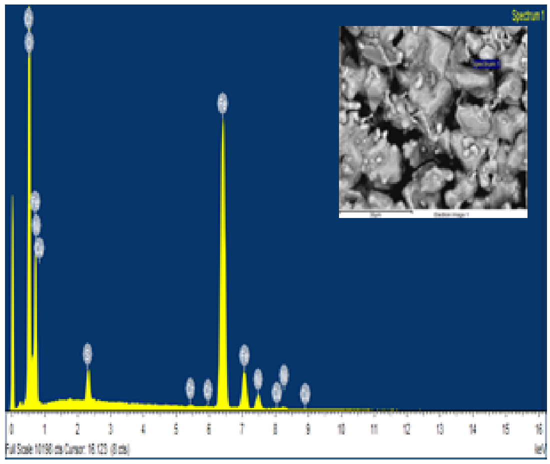

Figure 2 Cu segregation in micro alloyed steel with Ni/Cu=2.5.

Table 2 Spectrum processing of steel with Ni/Cu=2.5.

Elements	O	S	Cr	Fe	Ni	Cu
Weight	40.18	1.62	0.2	53.54	4.14	0.33
Atomic %	69.85	1.4	0.1	26.52	1.95	0.18

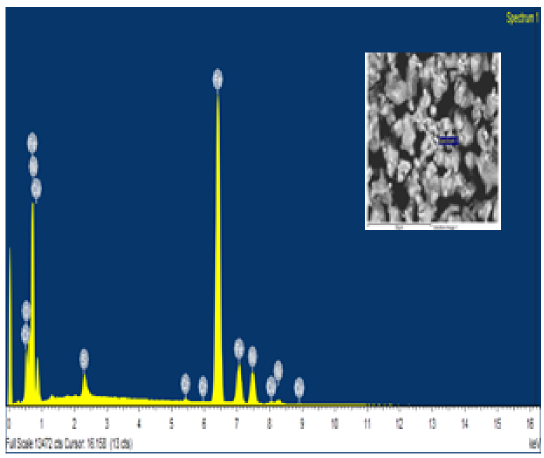

Figure 3 Cu segregation in micro alloyed steel with Ni/Cu=5.0.

Spectrum processing in **Table 3** shows total 100% and standard element detected to form different oxides in the scale such as iron oxide chromium oxide, nickel and copper oxides.

The SEM examination and EDS analyses of the oxide scale shown in the **Figures 2 and 3**, shows dimples containing inside particles of Sulphur inclusions surrounded by Cu segregation in both the cases.

Furthermore, the presence of copper around inclusions seemed to be less common in this steel [7,8].

This may help to explain the role of nickel in counterbalancing the harmful effect of copper, this investigation was focused to the problem of sulphide inclusions influencing the segregation of Cu and its consequence regarding the hot shortness and low ductility in steels.

Figures 2 and 3 shows that copper segregates around sulphide inclusions both in micro alloyed steels with low as well as high Ni/Cu ratio, both on the fracture surface and inside the matrix.

Table 3 spectrum processing of steel with Ni/Cu=5.0.

Elements	O	S	Cr	Fe	Ni	Cu
Weight	1.41	0.39	76.67	76.67	13.08	0.92
Atomic %	22.08	2.06	0.36	64.38	10.45	0.68

Cu precipitates as CuS but it also migrates to the sulphide inclusions forming segregation.

It is not clear whether it also segregates around inclusions not containing sulphur [8]. So addition of Ni modifies the sulphide inclusion which improves mechanical properties of steel.

XRD analysis shows Oxide Scale sample of higher Ni/Cu ratio were collected in powder form for phase identification by X-ray Diffraction (XRD) method. The XRD analysis was carried out by using PANalytical X'Pert PRO X-ray in Xpert software.

Diffractometer using Co-radiation at 40 kV/30 mA setting and Fe-filter. Line focus optics were used for the analysis. The XRD pattern for the scale sample with higher as well as lower Ni/Cu ratio is presented in **Figures 4 and 5**. Sample shows presence of mainly iron oxides viz. Fe_2O_3 and Fe_3O_4. First layer of oxide FeO is not present in the sample.

As observed from the relative intensities of 100% intensity peaks of Fe_2O_3 and Fe_3O_4 in the samples, it can be qualitatively said that the ratio of amount of Fe_2O_3 to Fe_3O_4 is more in sample in which Ni/Cu ratio is high [8].

Also to ensure how the scale thickness increases with increasing in Ni to Cu ratios, scale thickness measurement was carried out by using mat lab which shows graphical representation of scale thickness and Ni to Cu ratios [8].

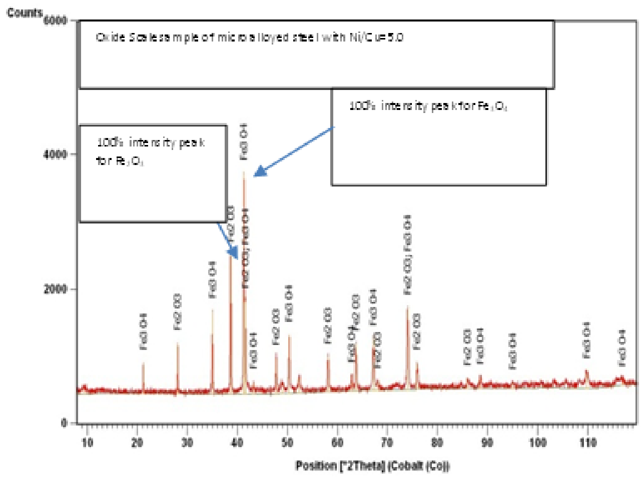

Figure 4 X-ray diffraction pattern of the steel (Ni/Cu=5) and phases observed are Fe_2O_3 and Fe_3O_4.

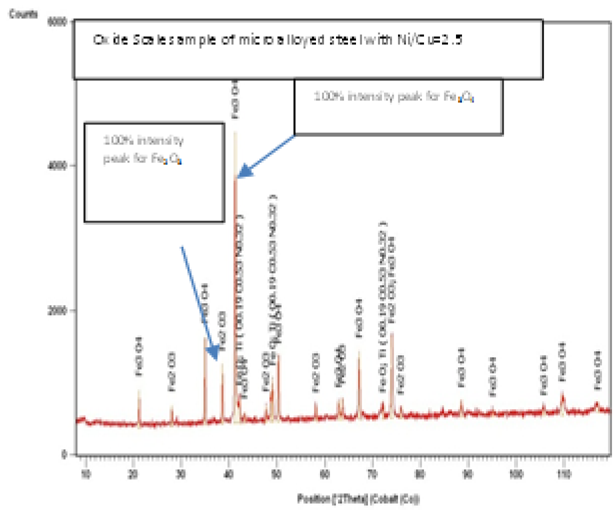

Figure 5 X-ray diffraction pattern for the micro alloyed steel (Ni/Cu=2.5) and phases observed are Fe2O3 and Fe3O4.

Figure 6 shows the oxide scale thickness comparison of various Ni/Cu ratios. The oxide scale formed on the sample after heating at high temperature. Scale/metal interface form on the samples is uneven. We can clearly see the difference in scale thickness. Thickness of oxide scale form on the higher Ni/Cu ratio is higher than that of all other samples having less than 2.5 Ni/Cu ratios.

Conclusion

- Experiment shows that the steel should contain Cu and Ni as low as possible. The Ni content should not be more than that of Cu as Ni forms uneven scale/metal interface.
- Ni/Cu ratio should be within 1 to 2.5. It should not exceed more than 2.5 as it increases the severity of cracking in surface.

- As ratio increases above 2.5 it results in increasing thickness of oxide scale on the micro alloyed steel surface at high temperature.

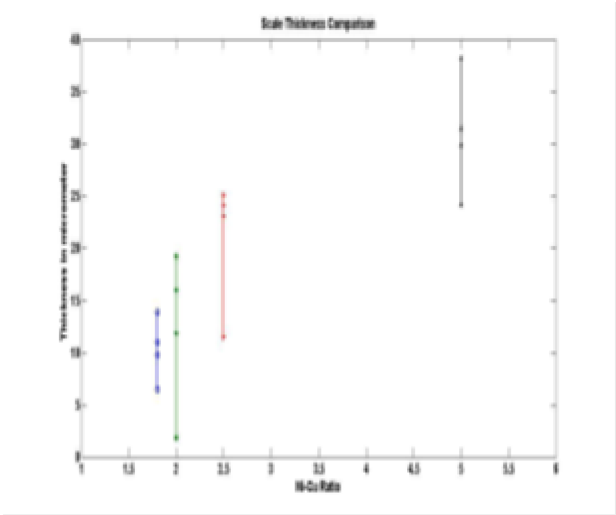

Figure 6 Scale thickness comparison.

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