1. INTRODUCTION

There has been much research regarding Mn-Ni alloys owing to their magnetic properties [1-3]. It has been shown that the manganese-nickel alloys in the form of thin foils can be employed for the brazing of nickel-based superalloys and stainless steel. Manganese provides good compatibility with nickel-based superalloys; it also acts as an effective melting point depressant [4-5]. Mn-30Ni filler alloy has been utilized for the brazing of stainless steels [6]. As for the corrosion resistance, Dean et al. has reported that these binary alloys have a tendency to tarnish rather quickly and to show premature evidence for general corrosion in the atmosphere as well as in an aqueous environments. Therefore, chromium is required to impart better resistance to atmospheric and general corrosion [4].

Brazing filler alloy is often used in very fine thickness (or diameter) in the form of foil (or wire). Therefore, deformation parameters particularly flow stress as a function of strain rate are very important in production process of brazing alloys. Arrhenius model has been applied for various alloying systems including Fe-Cr-Ni alloy [7], ultra-high strength steels [8], Al-Si alloy [9], Az24 magnesium alloy [10], AA785 aluminum alloy [11], and low carbon steel [12] to determine constitutive equation in order to predict flow stress. However, there is still a lack of experimental research focusing on the hot deformation behavior of Mn-Ni-Cr alloy. Hot compression behavior and its constitutive equation should therefore be considered to acquire an optimum temperature, strain rate and operation parameters of the hot rolling process, which are necessary to produce the filler brazing foil. Therefore, present investigation was carried out to determine a constitutive equation for the hot compression of the Mn-Ni-Cr alloy.

2. EXPERIMENTAL

Mn-25Ni-5Cr (%wt.) alloy was prepared by using Mn, Ni and Cr elements in a vacuum induction melting furnace under argon atmosphere. The cast ingots were homogenized at 950°C for 4 h. Cylindrical specimens with a diameter of 8...
mm and a height of 12 mm were machined from the ingots. To establish the stress-strain behavior of the alloy, uniaxial hot compression tests were conducted on a servo-hydraulic 500KN computerized material testing system equipped with a resistance furnace. The compression tests were performed in the temperature range of 700-900°C, and the strain rate was varied from 0.001 to 0.1 s⁻¹. The samples were heated at a heating rate of 10°C/min, and soaked for 10 min at the deformation temperature. The specimens were allowed to deform to half their original height and water quenched immediately. Fine grooves at the top and the end of specimens were machined to maintain lubricant until the final stages of the test. Therefore, the effect of friction was well controlled and barreling in the specimens was approximately prevented. However, friction effect was removed using equation (1):

\[ \sigma_a = \sigma_0 \left(1 + \frac{mD}{3\sqrt{3}H}\right) \]  

(1)

Where, \( \sigma_a \), \( \sigma_0 \), and \( m \) represent measured axial stress, effective flow stress, and the friction coefficient, respectively. The barreling parameter of each specimen was calculated using equation (2) and the friction coefficient was measured with the help of standard tables.

\[ B = \frac{h(r_{max})^2}{h_0(y_0)^2} \]  

(2)

The deformed specimens were sectioned parallel to the compression axis for further analysis. The thermal transition behaviour was studied under non-isothermal condition using NETZCH STA 409 PC/PG differential thermal analyzer (DTA). Samples for microscopic examination were prepared using the standard metallographic procedures and were etched using 10ml H₂O₂ + 10ml HCL + 1ml HNO₃ solutions. As-cast and heat treated samples were characterized by utilizing the Philips x-ray diffractometer (XRD) with a Cu-Kα radiation at 30mA and 40 kV.

3. RESULTS AND DISCUSSION

The true stress-strain curves obtained at various deformation conditions are illustrated in Fig. 1. It can be seen that the influence of temperature and strain rate on flow stress is significant. It could also be observed that the true stress-strain curves have three distinct stages. In the initial stages of formation, the flow stress increases considerably as the strain enhances to a peak value, suggesting that the hard working rate is higher than the softening rate. Then the true stress-strain curves are gradually decreased or even kept constant with a variety of softening rates. However, it could be seen that the flow stress significantly decreases with increasing the temperature from 700 to 750°C, suggesting a reduction in the strengthening mechanism of the alloy. The DTA graph of the alloy tested in the temperature range from room temperature to the melting point is shown in Fig. 2-(a). According to the Mn-Ni phase diagram (Fig. 2-(b)), the first and second peaks are related to the solid state transitions in the Mn-Ni phase system [13]. While the third one at 741°C might be attributed to formation of a single solid solution phase called \( \gamma \). To get further insight into this transformation, XRD analyses were performed. The XRD pattern of the specimen heat treated at 750°C for 1 hour and then quenched into water was compared with that of the as-cast alloy (Fig. 3).

![Fig. 1. The true stress-true strain curves of the alloy in the strain rate of (a) 0.1 s⁻¹, (b) 0.01 s⁻¹, and (c) 0.001 s⁻¹.](image-url)
Fig. 3. The X-ray diffraction pattern of the Mn-25Ni-5Cr alloy.

γ-Mn (Cubic) and Mn₃Cr (Tetragonal) phases were identified in the as-cast pattern. However, the intensity of the Mn₃Cr peaks decrease (or approximately disappear) in the heat-treated specimen. Since the atomic radius of chromium (166 pm) is very close to that of manganese (161 pm), the peaks related to γ-solid solution does not show noticeable shift due to the solution of the remaining chromium atoms. Moreover, DTA and XRD results reveal that the first endothermic peak at 741 °C represents the dissolution of the Mn₃Cr and the formation of the single solid solution phase. Our previous study on another alloy system showed that the intermetallic compounds could have a strengthening effect on flow stress and a detrimental effect on ductility [14]. Accordingly, the formation of a single solid solution and the removal of intermetallic compounds from the microstructure might be regarded as a possible explanation for reduction in flow stress at temperatures higher than 741 °C. Meanwhile, by comparing this transition temperature with the Mn-Ni phase diagram [13], it could be concluded that the addition of chromium led to an increase in the solid solution temperature from ~ 625 °C for the Mn-30Ni alloy to ~741 °C for the Mn-25Ni-5Cr alloy. It should also be mentioned that the heating rate of DTA analysis and heat treatment was relatively low (10 °C/min); therefore, the reason for such a difference in transition temperature cannot be related only to the effect of the heating rate. It was found that the last endothermic peak which was related to the melting point of the alloy was shifted to the higher temperature (from ~1035 to 1100 °C) in the Mn-25Ni-5Cr alloy.

Another point arising from Fig. 1 is formation of a single peak in the flow curves. Generally, the flow stresses could be rapidly raised with the strain increase in the early stage of isothermal compressive deformation. This was undoubtedly be due to the domination of work hardening. It has been found that as the dislocation density increases, the effect of work hardening balances out with dynamic softening, with a peak appearing in the flow curve [14]. In fact, one of the characteristics of stress- strain curves under the DRX condition is the appearance of a peak diminishing flow stress and then stabilizing the flow stress. Nevertheless, the stress-strain curves were dropped slowly with an increase of the strain after the peak, suggesting that the DRX process for this alloy was rath-
er sluggish. This could be attributed to the large amount of the alloying elements in this alloy which increases the SFE and therefore, promotes the recovery process. This type of behavior has also been observed in 904L austenitic stainless steel during the hot compression test [15]. Following the peak flow stress, the stress reached the steady state due to the balance between work hardening and flow softening. Meanwhile it could be seen from Fig. 4 (a) that the microstructure of the hot deformed specimen at 700 °C and 0.1 s⁻¹ contains both elongated (indicated by arrows) and equiaxed recrystallized grains indicating that partial dynamic recrystallization had occurred. However, no elongated grains were detected in the microstructure of the specimens deformed at 900 °C at the strain rate of 0.001 s⁻¹ and the new grains formed by DRX could be clearly observed. Also, our results showed that while the microhardness of the specimen, deformed at 700 °C and 0.1 s⁻¹ with the elongated grains (fig. 4-a), was 280±10 H.V, it was 200±10 H.V. for the specimen deformed at 900 °C and 0.001 s⁻¹ with fully equiaxed microstructure. This evidence confirmed microstructural observations and suggested that while dynamic recovery and partial recrystallization had been occurred at low temperatures and high strain rates, DRX was the dominant softening process at high temperatures and low strain rates.

On the other hand, from the flow curves it could be observed that the oscillation phenomenon had taken place at the low strain rate (0.001 s⁻¹). This is indicative of the fact that the alloy was completely recrystallized due to low strain rate and the high temperature. In a previous study done by the authors it was shown that higher temperature facilitates the formation of new grain boundaries and subsequently, low strain rate could provide the proper time for recrystallization [16-17]. Therefore, with the continuation of the deformation process, the alloy was hard worked, leading to a peak in the flow curves. Then, the softening process occurs and under these conditions, the amounts of flow stress oscillates during hot compression.

In order to further study the hot deformation behavior of the Mn-25Ni-5Cr alloy its deformation characteristics was investigated using a constitutive equation. Hot deformation of metallic materials is a thermal activation process and the strain rate is related to the temperature, the deformation activation energy, and the stress. Hot deformation is expressed by Arrhenius model as shown in the following equation [15]:

\[ Z = \varepsilon \exp\left(\frac{Q}{RT}\right) = A[\sinh(\alpha\sigma)]^n \]  \hspace{1cm} (3)

Where, A is a constant, \( \alpha \) is a temperature-independent material constant, \( n \) is a stress exponent, R is the universal gas constant, and Q is the activation energy for deformation. \( \sigma \) can be either peak stress or steady flow stress. In this paper, the steady flow stress was considered for calculation. It is generally accepted that the sine hyperbolic equation is suitable for constitutive analysis over a wide range of deformation temperature and strain rates [18-20].

To determine the constants by taking the natural logarithm from each side of the equation (3):

\[ \ln(\varepsilon) = \ln A + n\ln[\sinh(\alpha\sigma)] - \frac{Q}{RT} \]

\[ n' = \left(\frac{\partial \ln \varepsilon}{\partial \ln \sigma}\right)_T \]

\[ \beta = \frac{\partial \ln \varepsilon}{\partial \sigma} \]

\[ n = \frac{\partial \ln \varepsilon}{\partial \ln(\sin(\alpha\sigma))} \]

Where, \( n' \) and \( \beta \) are the average slope of \( \ln(\varepsilon) \) -\( \sigma \) and \( \ln(\varepsilon) -\ln(\sigma) \) lines at the constant temperature respectively. An approximate value of \( \alpha \) was calculated by \( \alpha = \frac{\beta}{n} \).

Fig. 5, Fig.6, and Fig.7 show \( \beta \), \( n' \), and \( n \) as obtained through the liner regression data; so the value of \( \alpha \) is 0.01468. It is obvious that the lines at
different temperatures are almost parallel; therefore, the correlation of the flow stress with the strain rate is slightly affected by temperature.

Rearranging Eq. (4) and differentiating with respect to $1/T$ result in an expression for the activation energy $Q$:

$$Q = \left[ \frac{\partial (\ln E)}{\partial \ln [\sinh(\alpha \sigma)]} \right] \left[ \frac{\partial [\sinh(\alpha \sigma)]}{\partial (1/T)} \right] E = R S$$  \hspace{1cm} (3)

Where $S$ is the average slope of the lines in the $\ln[\sinh(\alpha \sigma)]$ against $1000/T$ plots, as shown in Fig. 8.

The value of $\ln(A)$ is obtained from the intercept of the $\ln(Z)$ against $\ln[\sinh(\alpha \sigma)]$ plot, after calculation of the activation energy $Q$ using Eq. (5). Generally, the hot deformation activation energy represents a difficulty in plasticity deformation. In the current study, $Q$ is calculated to be 301.07 KJ/mol, which is higher than that for most conventional brass alloys [21] and lower than that for austenitic steel calculated by Pernis et al. [22]. It seems that the relatively high activation energy of the Mn-25Ni-5Cr alloy is the result of the high amounts of the solute alloying element in the Mn lattice.

On the other hand, the value of $A$ could be calculated, as shown in Fig. 9. To confirm the accuracy of the calculated parameters, the relationship between the measured peak stress $\ln(\sinh(\alpha \sigma))$ and the $Z$ parameter $\ln(Z)$ was plotted, as shown in Fig. 9. Regression analysis revealed that for this alloy, the correlation coefficient $R$ is higher than 0.92; this indicates that the proposed constitutive equations could provide a reliable estimate of the flow stresses.
By substitution of the values in Table 1 in Eq. 3, we will get the isothermal compression equations of the alloy, as shown in Eqs. (6) and (7).

\[ \varepsilon = 1.36203 \times 10^{12} \left[ \sinh(0.01468\sigma)^{4.8484} \right] \exp(-301072.4/R\theta) \]  
\[ \sigma = 1/0.0147\ln\left[\frac{Z}{1.36203 \times 10^{12}}\right]^{1/4.84} + \left(\frac{Z}{1.36203 \times 10^{12}}\right)^{1/4.84} + 1\]  

Table 1. Values of material constants of Mn-Ni-Cr alloy

<table>
<thead>
<tr>
<th>A(s⁻¹)</th>
<th>α(Mpa⁻¹)</th>
<th>n</th>
<th>Q(KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.36203×10¹²</td>
<td>0.0147</td>
<td>4.84</td>
<td>301.07</td>
</tr>
</tbody>
</table>

Fig. 9 - The relationship between ln Z-ln[sinh(ασ)]

A good agreement between the predictions of the equation 5 and the obtained results for the examined conditions (the strain rate 0.001 to 0.1 s⁻¹ and the temperature of 700 to 900 °C) signifies the applicability of the equations used for estimating flow stress at higher strain rates. On the basis of these obtained equations, the value of Z is desirable for the discussion of hot deformation in which T and ε₀ are known, whereas the flow stress is not measurable. According to the measured dissolution transition temperature (Fig. 2) and to reduce flow stress (Fig. 1), the temperature above 750 °C was selected for preheating in the actual rolling process of the alloy. Also, the strain rate was calculated according to the following equation applied in a similar research by Kratochvil et.al. [23]:

\[ \varepsilon = 2/\sqrt{3} \left( \frac{\nu}{\sqrt{R(H_0 - H_i)}} \right) \varepsilon_h \]  

Where, H₀ and H₁ (mm) refer to the thickness of the specimen before and after rolling, εₕ is the true strain, ν (mm/s) is the peripheral velocity of the rolls, and R is the roll radius. The values of strain rate used in the equation 1 to calculate Z. Finally, the required stress for hot rolling was predicted by the equation 5. The observations of the actual hot rolling process of the alloy verifies that the maximum total reduction (MTR) up to 87% could be achieved by applying theses parameters.

4. CONCLUSIONS

In this study, the deformation of the Mn-25Ni-5Cr alloy was investigated at the deformation temperature of 700-900 °C and the strain rates of 0.001 to 0.1 s⁻¹. The following conclusions were drawn from the results obtained:

1. The flow stress of the alloy was affected by the temperature; the difference was particularly significant between 700 and 750 °C. The stress-strain curves, DTA and XRD results also showed that the flow stress of the alloy dramatically decreases at 750 °C due to the dissolution of Mn₇Cr phase and the formation of a single solid solution.

2. The stress-strain curves at low temperature and high strain rate were dropped slowly while the microstructure of the deformed specimens contained some remaining elongated grains. However, by increasing the temperature and decreasing the strain rate, dynamic recrystallization was clearly observed in the specimens. It is concluded that by reducing the value of the Z parameter, dynamic recrystallization could overcome the dynamic recovery.

3. The level of the flow stress of the Mn-25Ni-5Cr alloy could be described by a hyperbolic-
ic-sine constitutive equation with the deformation activation energy of 301.07 kJ/mol, and also by a Zener-Holloman parameter.

REFERENCES